MIAMI BEACH, FLORIDA
JUNE 11-13, 1952
ST. MORITZ HOTEL

REPORT OF

marine borer conference

SPONSORED BY

THE WILLIAM CLAPP LABORATORY
THE MARINE LABORATORY, UNIVERSITY OF MIAMI

THE MARINE LABORATORY

UNIVERSITY OF MIAMI

CORAL GABLES 46, FLORIDA

APRIL 1953

LIST OF PARTICIPANTS REGISTERED AT THE MARINE BORER AND PREVENTION OF DETERIORATION IN WATER-FRONT STRUCTURES CONFERENCE, HELD AT MIAMI BEACH JUNE 11-12-13, 1952

Alexander, Allen L.
Naval Research Laboratory
Code 3220
Washington 25, D. C.

Alumbaugh, Robert L.
U.S. Naval Civil Engineering Lab.
Port Hueneme, California

Allen, Henry
Allen Cathodic Protection
P. O. Box 386
Harvey, Louisiana

s, J. R.
ynolds Metals Company
00 S. 3rd Street
uisville, Kentucky

ews, J. W.
. S. Steel Company
esearch Laboratory
34 Atwood Street
ittsburgh 13, Penna.

ell, H. W.
merican Lumber & Treating Co.
32 So. Michigan Avenue
hicago, Illinois

ne, Bowman F., President
The University of Miami
Coral Gables, Florida

Barnes, A. H., Lt.
Bureau of Yards & Docks
U. S. Navy Department
Washington 25, D. C.

Beal, James A.
U. S. Department of Agriculture
Agricultural Research Center
Beltsville, Maryland

Bernuth, E. P.
Bernuth Lembcke Co., Inc.
420 Lexington Avenue
New York, New York

Boynton, E. P.
National Cylinder Gas Company
840 N. Michigan Ave.
Chicago 11, Illinois

Chuck, Frank
Creole Petroleum Corp.
Cabimas, Estado Zulia
Venezuela, South America

Colley, Reginald H.
Bernuth Lembcke Company
420 Lexington Avenue
New York, New York

Collier, J. T.
The Barrett Division
Allied Chemical & Dye Corp.
40 Rector Street
New York, New York

Davis, C. Hubbard
Sub-Tropical Testing Service
3371 S.W. 1st Avenue
Miami, Florida

Dickie, Roy N.
U. S. Coast Guard
2610 Tigertail Avenue
Miami 33, Florida

Fuller, R. Glen
Battelle Memorial Institute
2244 S. Halifax Drive
Daytona Beach, Florida

Fulton, Clarence O.
B. C. Research Council
U. B. C. Campus
Vancouver, B. C.

Galler, Sidney R.
Head, Biology Branch
Office of Naval Research
Department of the Navy
17th St. & Constitution Ave.
Washington 25, D. C.

Garrett, John H.
Research & Development Board
The Pentagon
Washington 25, D. C.

Gehrke, Walter A.
U. S. Navy Department
Naval Station
New Orleans, Louisiana

German, J. P., Comdr.
U. S. Coast Guard
2610 Tigertail Avenue
Miami, Florida

Gifford, Charles A.
The Marine Laboratory
University of Miami
Coral Gables, Florida

Gordon, E. S., Comdr.
U. S. Coast Guard
2610 Tigertail Avenue
Miami 33, Florida

Greenfield, Leonard J.
The Marine Laboratory
University of Miami
Coral Gables, Florida

Greenwald, J. A., Jr.
Cuprinol Division
Darworth Inc.
Simsbury, Conn.

Harrington, Jr., Earl W., LCdr.
U. S. Navy Department
District Public Works Office
Fifth Naval District
Norfolk, Virginia

Hearst, Peter J.
U. S. Naval Civil Engineering
Research and Evaluation Laboratory
Port Hueneme, California

Heiks, Ray E.
Battelle Memorial Institute
Columbus, Ohio

Hennacy, Richard A.
The Marine Laboratory
University of Miami
Coral Gables, Florida

Hill, E. G.
British Joint Services Mission
Main Navy Building
Washington, D. C.

Hinchman, Wm. H. D.
The Hinchman Corp.
1207 Francis Palms Bldg.
Detroit, Michigan

Holden, Edward R.
U. S. Naval Civil Engineering
Research and Evaluation Laboratory
Port Hueneme, California

Hood, Donald W.
Texas A & M College
College Station, Texas

Isham, Lawrence B.
The Marine Laboratory
University of Miami
Coral Gables, Florida

Jelley, J. F., Rear Admiral
Chief, Bureau of Yards & Docks
U. S. Navy Department
Washington 25, D. C.

Jones, Morris T.
Office of Naval Research
844 No. Rush Street
- Chicago, Illinois

Jones, W. A., Jr.
U. S. Steel Company
Coal Chemical Sales
525 Wm Penn Place
Pittsburgh, Penna.

Kaeser, F. L.
Todd Shipyards Corp.
1 Broadway
New York, N. Y.

Kartinen, Ernest
Signal Oil & Gas Company
811 West 7th Street
Los Angeles, Calif.

Kelly, A. W., Jr.
Wood Treating Chemical Co.
5137 Southwest Avenue
St. Louis 10, Missouri

Knox, George E.
Bureau of Yards & Docks
U. S. Navy Department
Washington 25, D. C.

Lane, Charles E.
The Marine Laboratory
University of Miami
Coral Gables, Florida

Lambert, W. P.
U. S. Navy Department
13th Naval District
Seattle, Washington

LaQue, F. L.
The International Nickel Co., Inc.
67 Wall Street
New York, New York

Larrick, Lewis
Office of Naval Research
U. S. Navy Department
Washington 25, D. C.

LeMay, Edwin P.
Captain Edwin P. LeMay & Associates
11th Floor, Pacific Bldg.
Miami, Florida

Loose, Hugo J.
Captain Edwin P. LeMay & Associates
11th Floor, Pacific Bldg.
Miami, Florida

Mann, Ralph H.
American Wood Preservers Assoc.
60 E. 42nd Street
New York 17, New York

Mark, William R., Jr.
U. S. Navy Department
5th Naval District
Norfolk 11, Virginia

Mayfield, P. B.
Barrett Division
Allied Chemical & Dye Corp.
40 Rector Street
New York, New York

McKennis, Herbert
U. S. Naval Civil Engineering
Research and Evaluation Laboratory
Port Hueneme, California

Meyer, Fred J.
The Dow Chemical Company
Midland, Michigan

Meyers, James F.
Port of New York Authority
111 Eighth Avenue
New York 11, New York

Otley, V. C.
The Barrett Division
Allied Chemical & Dye Corp.
40 Rector Street
New York, New York

Parson, A. F., LtCdr.
U. S. Navy Department
D.P.W.O. 13th Naval District
Seattle, Washington

Paterson, H. T.
The International Nickel Co.
P. O. Box 262
Wrightsville Beach, N. C.

Reed, W. D.
Dept. of Army Engineers
Office of the Chief of Engineers
Bldg. T-7, Room 2041
Washington 25, D. C.

Reside, James T.
Bureau of Yards & Docks
U. S. Navy Department
Washington 25, D. C.

Richards, A. P.
W. F. Clapp Laboratories
Duxbury, Massachusetts

Ritter, J. R.
U. S. Navy Department
D.P.W.O. 12th Naval District
San Bruno, California

Roche, James N.
Creosote-Pitch Sales
Koppers Company, Inc.
Pittsburgh, Pa.

*

Sedlack, Frank
United States Steel
Pittsburgh, Penna.

Scheltema, Rudolf S.
Chesapeake Biological Laboratory
Solomons, Maryland

Sharpnack, E. V., Sr.
Reynolds Metals Co.
2500 So. Third St.
Louisville, Kentucky

Shaver, A. H.
Bureau of Yards and Docks
U. S. Navy Department
San Francisco Naval Shipyard
San Francisco, Calif.

Shoemaker, Tom L.
Philadelphia Naval Shipyard
Philadelphia 12, Penna.

Sims, Rudolph W.
The Marine Laboratory
University of Miami
Coral Gables, Florida

Smith, F. G. Walton
The Marine Laboratory
University of Miami
Coral Gables, Florida

Sprugel, George, Cdr.
Asst. Head, Biology Branch
Office of Naval Research
U. S. Navy Department
Washington, D. C.

Stokes, Ralph C.
Bureau of Yards & Docks
U. S. Navy Department
Washington, D. C.

Sturrock, Murray G.
Koppers Company, Inc.
1246 Koppers Bldg.
Pittsburgh, Penna.

Sweeney, T. R.
Naval Research Laboratory
Washington, D. C.

Swildens, Lawrence
Timber, Inc.
15 N.W. South River Dr.
Miami, Florida

Thomas, Arlo
Hdqtrs., 11th Naval District
San Diego 30, California

Thompson, A. J.
6th Naval District
P. O. Box 365
Charleston, S. C.

Tonneson, Russell S., Cdr
U. S. Navy Department
3rd Naval District
90 Church Street
New York, New York

Van Etten, Frank M.
Bureau of Ships
U. S. Navy Department
Washington, D. C.

Volkening, V. B.
Dow Chemical Company
Freeport, Texas

Voripaieff, A. N.
A. M. Byers Company
30 Rockefeller Plaza
New York 20, N. Y.

Voss, Gilbert L.
The Marine Laboratory
University of Miami
Coral Gables, Fla.

Voss, Nancy
The Marine Laboratory
University of Miami
Coral Gables, Fla.

Wangaard, F. F.
Professor of Forest Products
Yale University
205 Prospect St.
New Haven, Conn.

Warren, J. R.
Duke University
Durham, North Carolina

Weber, Carl
420 Lexington Ave.
New York, New York

Wessel, Carl J.
National Research Council
2101 Constitution Ave.
Washington 25, D. C.

Wright, K. E.
Bureau of Yards & Docks
U. S. Navy Department
Washington 25, D. C.

Wymer, W. H.
U. S. Navy Department
Box "P" Hdqtrs, 15 Naval Dist.
Navy No. 121, F.P.O.
New York, New York

* Roe, Thorndyke, Jr.
U. S. Naval Civil Engineering
Research & Evaluation Laboratory
Port Hueneme, Calif.

- - - - - - - -

FOREWORD

Success of the Marine Borer Conference held at the U. S. Naval Civil Engineering Research and Evaluation Laboratory on May 10-12, 1951, led to a general agreement that similar conferences should be held annually. Accordingly, arrangements were made for a meeting to be held in 1952 at Miami Beach. The program was subsequently organized by The Clapp Laboratories, in cooperation with the Marine Laboratory of the University of Miami. The generous assistance of many persons contributed to the success of the program and especial credit is due to Mr. George Knox of the Bureau of Yards and Docks for his energetic and valuable cooperation.

Limited time and clerical assistance have not only delayed publication of the report of the 1952 meeting, but, in order that this delay should not be further extended, manuscripts have been processed without submission to the authors for correction. Minor changes have been made in order that all papers should be presented uniformly, in the third person, and in written rather than spoken form. The editor accepts full responsibility for errors, and tenders his apologies to the authors for mistakes that may inadvertently have crept in.

F. G. Walton Smith

F. G. Walton Smith

The Marine Laboratory
University of Miami
Coral Gables, Florida

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ADDRESS OF WELCOME

by Dr. Bowman Foster Ashe
President of the University of Miami

OBITUARY

The death of Dr. Ashe on December 16, 1952, was a great loss to the whole field of education as well as to the University of Miami, in which his personality is firmly implanted.

The opportunity is taken of paying a special tribute to the memory of Dr. Ashe for the part he played in developing research in the marine sciences. Under his leadership and aided by his constant encouragement, the Marine Laboratory of the University of Miami came into being in 1943 and has grown continually in the past decade. The field of underwater deterioration including the control of marine borers, has been of especial interest to the Laboratory since its inception and it is fitting that one of Dr. Ashe's last official acts should have been to welcome delegates to the Marine Borer Conference.

Obituary

A scroll with the following text was introduced by Frank L. LaQue and George E. Knox and by unanimous resolution of the assembled delegates was presented to Mrs. Clapp.

DR. WILLIAM F. CLAPP

WHEREAS, Dr. William F. Clapp, renowned educator and marine biologist, whose death occurred on December 28, 1951, was a member of our group and the winner of many merited honors during his activities in the studies of marine borers; and

WHEREAS, Dr. Clapp's distinguished record as a marine biologist, and his enthusiasm and devotion to the interests of this group have contributed greatly to its success during five years of its organization; and

WHEREAS, in his death the group has lost not only an old and valued member but a true friend whose memory will be long cherished by all who knew him; therefore be it

RESOLVED, that the Marine Borer group in its Fifth Annual Meeting assembled expresses its profound sorrow at the loss of its esteemed member and friend; and be it

RESOLVED, that the Marine Borer group extend to Dr. Clapp's family its deepest sympathy in their bereavement; and be it

RESOLVED further, that this resolution be published in the Journal of the Sea Horse Institute and other suitable scientific publications and that copies be sent to Mrs. Clapp

Frank L. LaQue George E. Knox

Miami, Florida. June 11, 1952.

(Contribution from the Office of Naval Research)

OFFICE OF NAVAL RESEARCH INTEREST IN PREVENTION OF DETERIORATION IN MARINE STRUCTURES

by Rear Admiral C. M. Bolster[1]

The interest of the Office of Naval Research might be stated thus:

> "The Navy encounters deterioration of its wooden marine structures; the prevention or alleviation of this deterioration requires research effort; that is our business."

But this is oversimplification; it will be better to trace the development of our interest. Let us start with the basic Act of Congress establishing the Office of Naval Research (ONR). Paraphrasing that Law slightly, it is charged with the encouragement, promotion, planning; initiation, and conduct of naval research in augmentation of and in conjunction with the research and development conducted by the respective bureaus and other agencies of the Navy Department.

Research interest is not born full blown as Venus was thought to be but grows at a recognizable pace, usually as research scientists develop ideas. In developing the background and growth of our interest it is not necessary to go back to the day when man first went down to sea in wooden ships nor to claim that when John Paul Jones founded the U. S. Navy he encountered this deterioration of his vessels and harbor structures.

There is no need to return even to 1924, when the National Research Council (NRC) published Atwood and Johnson's book, MARINE STRUCTURES - THEIR DETERIORATION AND PRESERVATION. Instead, a start will be made with the forerunner of the Office of Naval Research.

In those crucial early days of World War II, the Navy Coordinator for Research and Development requested the President's Office of Scientific Research and Development (OSRD) to establish working groups to assist in overcoming the terrific problems being encountered in the deterioration of materials in the tropics. The OSRD Tropical Deterioration Center (Glenn Greathouse, Director) operated from 1942 to 1945. When OSRD was disbanded in 1945, the Navy contracted with the National Academy of Sciences through the newly established Office of Research and Inventions for the establishment of the National Research Council - Prevention of Deterioration Center (NRC-PDC). The date of this contract, our first official venture in this field, was 1 December 1945.

[1]Delivered by Dr. Lewis Larrick, Office of Naval Research.

One of the first actions of the NRC-PDC was the initiation of a contract with the Wm. Clapp Laboratories for marine-borer studies. In August 1948 direct administration of this contract project was assumed by what is now the Organic Materials Branch of ONR.

Another early activity of the PDC was the formation of the National Defense Deterioration Prevention Committee, an important sub-group of which was the Marine Borer Panel. If it is recalled correctly, George Knox served as Chairman of the Panel until the disestablishment of the whole committee. One result of the several valuable meetings of this Panel was the establishment of a project by the Organic Materials Branch of ONR with the University of Miami on Marine Borer Research, in cooperation with the Bureau of Yards and Docks.

The Prevention of Deterioration Center has sponsored, under its ONR contract, a number of conferences in the broad field of prevention of deterioration of materials. Of particular importance to this discussion are the following:

> July 1949, West Coast Conference, in cooperation with the California Academy of Sciences.
>
> June 1950, Wrightsville Beach Marine Conference, in cooperation with Frank LaQue's group.
>
> 1951 West Coast Conference, May 1951, Pt. Hueneme, sponsored by BuDocks.

Immediately following the 1950 Wrightsville Beach Conference, a series of internal Navy conferences were held on a question raised there - the creosote problem. A Navy research program on creosote was initiated at these conferences in 1950. Dr. Alexander started a project at NRL on the characterization of creosote. He reported on progress last year at Hueneme; Dr. Sweeney has a further report to make later in this conference[1]. In setting up this program back in 1950 (and the plans agreed on them are still being followed), a biological assay phase of the creosote program was planned, to be initiated when Alexander's and Sweeney's characterization studies warranted; this biological assay phase is now active at the Marine Laboratory of the University of Miami. Dr. Walton Smith and his colleagues are going to discuss work pertinent to the creosote program during this conference[2].

In this historical sketch, the fact should not be overlooked that the Marine Borer Panel considered reports about the extraordinary marine-borer resistance of some tropical woods. Accordingly, the ONR Tropical Woods Project at Yale School of Forestry, directed by Professor F. F.

[1] See Section S
[2] See Sections J, L, P, Q

Wangaard, was brought into this program. He ill probably mention the durable tropical American woods that are available. Perhaps he will be able to give some indication why some of them are resistant to marine borers[1].

The background chronology has been sketched in order to show you how research interest grows and how diverse methods of attack are employed on the problem: direct laboratory work such as at NRL, conferences and scientific meetings such as this, contract projects with outside agencies, and bringing into participation other investigators who may have been working in other related areas. Before discussion of ONR's current program and plans, it may be well to mention the organization and method of operation.

Established on 1 August 1946 by Act of the Congress, ONR is the immediate successor of the Navy's Office of Research and Invention, and its predecessor, the Office of the Navy Coördinator for Research and Development. The pertinent section of our basic charter has already herein been paraphrased. Two units of the Office are involved in the problem of this Conference. It is unnecessary to say much about the Naval Research Laboratory. It is a large laboratory with about 4000 people devoted to the conduct of basic and applied research for the Navy Department.

The other unit is what is called, by those belonging to it, the Research Group, perhaps because the nearest to an official title is "The Assistant Chief of Naval Research for Research." Its primary mission is to encourage, support, and coordinate research activity in augmentation of and in conjunction with the research and development conducted by the bureaus and other agencies of the Navy Department - in other words, to operate the contract research program of ONR.

Operating with research scientists in the universities, nonprofit and industrial laboratories, and other government agencies (including Naval laboratories), the staff of the Research Group is composed chiefly of individuals selected from the scientific disciplines: physics, mathematics, chemistry, biophysics and biochemistry, and other divisions of biology, including ecology. There is also a staff of specialists (not called engineers) in such fields as electronics, acoustics, power, and materials. In addition, the Navy keeps a group of line and engineering officers on duty in the Research Group as liaison with the problems of the Fleet.

In operating this broad contract research program the Scientific Officers try to keep abreast of current and anticipated Naval problems and of the research activity and potential of the Nation. They do not originate research ideas, plan projects, or direct research activity. They consult with research scientists, review proposals, administer the scientific aspects of approved projects, and interpret research results for colleagues

[1]See Section T

in the Navy Bureaus and other agencies of the Department of Defense.

Any qualified scientist may present a proposal for a research project, but certain information is required before it can be considered (copies of the Research Proposal Guide are available here for interested persons). Each proposal received is reviewed by the staff of the Research Group and by their consultants and advisory committees, for scientific merit and potential. If the proposal - the property of the investigator - meets ONR standards, if the proposed work fits into the planned program, and if there are funds available, a contract is negotiated with the business organization with which he is affiliated. It is important to note that "a contract is negotiated," not "an award is made."

Progress is maintained not only through ONR's own private meetings with the investigators and internal reports but also through publication and presentation of papers. Early dissemination of research information to the scientific profession is considered necessary and his colleagues' discussions are used in measuring an investigator's progress.

The source of ONR's concern with this problem lies in the materials group and, since wood is an organic material, in the Organic Materials Branch. However, it is felt that research projects should be administered, as well as conducted, by individuals skilled in the arts and techniques required. Accordingly, the most of the contract projects in this area are, and will continue to be, administered by the Biology Branch. Dr. Galler and Dr. Sprugel are both here to participate in this conference.

Returning to the direct subject of this talk, the interest of ONR in the Prevention of Deterioration in Marine Structures and, specifically, in marine borers, is materialistic: ONR is trying to help the Navy obtain the most durable wooden structures possible, to find the most durable woods available in the Western hemisphere, to improve the methods of treatment (impregnation) of wood, to improve the treating agents and to obtain better and cheaper treatments.

The problem is approached from several angles, keeping in mind that participation will be principally in the basic research phases of the program, and contributions will be from the sciences and technologies whence the research ideas originate. Among the elements of the ONR contract research program which may be called upon are:

Organic chemistry: the synthesis of toxic and/or repulsive compounds

Physical chemistry: characterization of the world standard - creosote - and identification of its active constituents

Enzyme chemistry: investigations of the enzyme systems of the destructive organisms and enzyme inhibitors

Physiology: functions of normal organisms

Ecology: habits, geographic distribution, and population fluctuations of marine pests

Oceanography: physical, chemical, and biological characteristics of infested areas.

Organic materials: tropical woods, protective coatings, etc.

Interest is not limited to the shipworm; he is merely the start. Before he has been finally eliminated as an enemy, attention will be turned to the other "borers," as scientific interest among research investigators and availability of funds make it possible.

To return to an earlier statement, ONR has a definite interest in the problem of the prevention of the deterioration of marine structures. A number of angles of attack are proposed and the problem is considered to be

1. to learn why and how marine organisms attach themselves to or damage wood;

2. to learn why and how such chemical complexes as creosote protect wood from attack;

3. to synthesize or develop agents or methods of protection which will keep the pests away from wooden structures.

ONR's objective is to prevent deterioration whether such prevention is obtained mechanically, biologically, or through toxic action.

(Contribution from the Bureau of Docks)

DETERIORATION PROBLEMS IN MARINE STRUCTURES

by J. T. Reside

The following paper should be classed as that of an experienced maintenance engineer who looks over everything that comes along but who must be very careful not to be led astray by some conscientious but probably overenthusiastic salesman or scientific fellow who thinks he has the last word in some process or gadget. Money for new construction and maintenance comes hard these days. When dealing with a plant like BuDocks, the value of which aggregates several billion dollars it is necessary to take the "doubting Thomas" attitude because of the damage which can be done by a wrong move. This should not be carried to the point, however, where new and helpful processes and materials would be unduly ignored because sometimes they can be the means to big savings in manpower and cost. Although by no means ignorant about new construction, the author does not propose in this talk to get into that field too deeply because one of the Bureau's staff who follows is well qualified and prepared to get into certain phases of that and it is probably best left to him[1]. Therefore, this paper will be given from the viewpoint of a maintenance engineer who has perhaps something worth while and interesting in the way of personal experience to offer, who is willing also to listen to others, and who is looking for information. This line of approach will give a quick picture of some of our fields of interest and some idea of our typical problems and the remedial measures adopted by BuDocks. The interest and help of the delegates present is sought in fields where satisfactory solutions to our problems have not yet been obtained.

Field of Interest

The field of interest is extremely broad technically including as it does as examples, piers, wharves, graving and floating dry docks, marine railways, floating cranes and floating power plants, pile drivers, dredges, buoy, anchor and chain moorings, etc. This field of interest is also world-wide in scope also and thus it is possible to give only a quick and brief picture of it in the time available here. It should, however, be enough to show what our problems are and where, if possible, members of this group may be of help. BuDocks is always willing, of course, to exchange information with anyone with similar problems and does do quite a lot of this with other Bureaus and offices, commercial concerns and also foreign countries, particularly the British.

By marine structures is not necessarily meant only those structures which are actually in the water but rather all structures, whatever

[1]See Section G

their character, which are exposed to severe water front conditions. For instance, a radio tower exposed to salt spray and wind-blown sand might give just as much if not more trouble than, let us say, a mooring buoy with its ground tackle which is actually in the water all the time except when it is lifted and taken ashore for overhaul. BuDocks has had actual examples of just such cases. There are paint coatings which are readily applied to moorings and which will hold them in reasonably good condition for quite some time but these same coatings are not practicable for application to radio towers and probably would not hold up even if they could be applied. Incidentally, it has been found that the only thing to do with towers so exposed is to paint them more frequently with our standard structural steel paint coatings with a higher content of zinc oxide to harden the surface of the paint. Typical locations where this has been necessary are Portsmouth, N. H., and Key West, Florida. This same tower problem occurs in buildings, vehicles, cranes, railroad stock, etc.

Getting right down to structures directly exposed to wind and waves, however, and with particular reference to salt water exposure, there are many problems running from the attacks of marine organisms on treated and untreated timber structures, both fixed and floating, with which this body is probably most concerned, to those having to do with corrosion of steel and deterioration of concrete and again, strange to say, in both fixed and floating structures.

Taking up the first of these subjects, long personal experience in Navy construction work has amply testified to the terrible damage done by marine borers. These pests are to be combatted all the time, but it is when they invade new areas as they are apt to do at any time, that they probably give us the most trouble. There are cases like the sudden attack on the timber structures at the Mare Island Naval Shipyard in the 1920's when prolonged up-country dry spells changed the salinity of the upstream waters thus permitting the borers to invade and live in waters not formerly suitable for their existance. Such an attack could and does literally put a Navy Yard water front out of commission and if it should come during a period of emergency a very serious situation would result. Sometimes too, like at New York, where the harbor waters are so polluted by sewage and industrial wastes as to eliminate the action of borers when and if anti-pollution measures are put into effect and are effective, it is necessary to watch out for timber waterfront troubles of all kinds. These examples point to the need for continuous study of new construction and applications to existing structures to render them immune to borer action which will be well covered later. At the same time, studies on marine borers must continue to seek the best means of limiting their depredations where it is not practicable or economical to build such applications into the structure originally. A typical problem of this type is the protection of the interiors of timber floating dry docks. The permanently exposed exterior salt water surfaces can be and are protected in the conventional manner, i.e., by the application of tar, Irish felt and creosoted sheathing. These measures are not very practicable internally, of course,

so it is necessary to depend on other measures such as the application of copper sulphate solutions, live steam, etc. Such applications and particularly when combined with a thorough going follow-up inspection system are very helpful but there is need for more positive means of control of these pests in this type of structure. Marine borer damage can be dangerous on any water front structure but it is probable that the maximum danger comes on a structure like a large timber floating drydock where the interiors of ballast tanks are not readily accessible for inspection and where the structure is working and heaving practically all the time due to wind, current and wave action and the strains from the handling of ships therein which can be very serious depending on how carefully the dock is handled. Difficulties flowing from these conditions, as in other marine structures, sometimes require a reduction in lifting capacity and possibly even taking the dock out of commission. Repairs, when they become necessary, are extremely difficult and expensive to make and may be practically impossible without complete rebuilding. Small wonder, therefore, that there is a decided preference today for steel and also reinforced concrete for floating dry dock construction. Timber still is a good building material for such structures for certain types of work, however, but unless we can come up with better interior control methods, the tendency will be steadily away from the use of timber. Because of this and the further fact that there are still quite a few Navy-owned timber floating dry docks, continued methods of control are so important. Dry rot and checking give us lots of trouble also in our timber floating dry docks and blocking for both floating and graving docks and marine railways. The first of these is very difficult and costly to correct as it almost occurs in complicated and more or less inaccessible areas and depending on the location where it does occur, it can result, as in the case of marine borer action, in restrictions in the use of the dock. So far, replacement of the affected timbers is the only remedy available to us in the correction of this trouble.

Our drydock blocking deterioration problem largely involves checking, and while this may seem trivial, it is actually not. The trouble here has been partially met by binding or strapping the blocks with steel angles or bars, which is expensive, and painting the ends of the blocks with heavy paint or coal tar or other bituminous coatings. This checking trouble and the general scarcity of suitable blocking materials has forced the Bureau to go to the use of concrete for blocking to a large extent. The Bureau has been experimenting lately with laminated blocking and with some signs of success. This problem of blocking deterioration is a serious one in our active docking facilities and in connection with laid-up docks the non-availability of blocking might well be the controlling element in placing such docks back in service in an emergency. It is a cause for serious concern even now on docks being returned to service but if they all had to be recommissioned in a hurry, the problem would be much more acute. Here then are other areas where we need study and help and particular attention is directed to helping the Bureau with the laminated blocks because something like

that is what will be necessary to use since big heavy hard timbers are harder to get all the time. Perhaps plastics can be made to serve here, as they are doing elsewhere.

Going on to our steel structures the big problem which is always present is corrosion. This can come about because the structure is always submerged or partially submerged in salt water as in the case of a steel pile pier, floating dry dock, derrick, pontoons, barges, etc. and also where the structure is not submerged but contains water on the inside; and do not minimize this second category either because sometimes it is even almost more unbeatable than the other. An example is a structure like a submarine escape training tank, such as the one at New London, Connecticut. This is a steel tank structure 20' in diameter and 100' high with an operating building on top and locks on the side at several points and a section of a submarine built in at the bottom. To minimize troubles here, fresh water is used as an operating medium but the local river water is slightly brackish at times, contains hospital and factory wastes, the inside tank surfaces must be white or some other light color for maximum safety. The medical personnel insist that the water be heated, filtered and chlorinated and because a diving bell operates therein with strong lights and telephones, there is, it seems, every factor making for a difficult steel surface protection job. A great many paint coatings were tried out in this tank before one was found which would hold up for any reasonable length of time and this one costs us about $12.00 per gallon for the final cost. All the coatings studied here have been catalogued and this information is available to interested parties.

It is pleasant to report, however, that all our steel protective coating problems are not as tough as that one but even so, they are immensely difficult to cope with and are complicated by a factor mentioned previously in this paper and that is by the great range of climatic conditions encountered. By this is meant that a bituminous coating for instance, which would hold up fine in a hot climate like Mobile, Alabama, would not do so well or might even fail completely if the same type structure on which it was used is built in or moved to the Arctic. In fact, this very condition has been experienced and must therefore be taken into consideration at all times when steel structures are built.

This matter of corrosion starts with construction and in floating structures at least brings up the old argument of pickling versus mechanical cleaning. In general, commercial practice is followed and pickling not used. But, on the other hand, a firm belief is held in a most thorough cleaning job including flame and mechanical cleaning, sand blasting, etc., where required. For combat vessels, by comparison, pickling is standard practice with a minimum of mechanical cleaning afterwards. Both methods seem to provide us with a good long-life floating craft but it is desired to know which system is the better. Since a lot of extra expense is involved in both systems, a present day evaluation of the two methods is desirable and that problem is presented here as one well worthy of some study.

Cleaning should also be studied to develop improvements in both methods and materials and to determine if overall savings are possible. This is important because cleaning is expensive at best, and it is uneconomic to insist on doing something just because it has been standard practice in the past. While we are on this subject of cleaning, it must not be forgotten that it is always present and for a much longer time during the usage stages of our structures and it is at that time that it really presents the biggest problem. This for the added reasons that inaccessibility and a deteriorated condition now present further complications. Many methods of cleaning which are entirely feasible on a new and relatively clean structure are totally inadequate when applied to a structure which is covered with varying thickness of rust and almost every known form of tuberculation and fouling and with deep pits due to corrosion or incorrect field welding practice. When cleaning under such conditions is considered, the uncertainties thereof and also the uncertainties of good results from the later application of protective coatings will be easily realized.

Before considering coatings or treatments in lieu thereof, the question of pre-coating treatments arises; that is, whether or not an inhibiting solution such as sodium dichromate and phosphoric acid should be used. This is standard practice in pickling operations and some authorities insist that such a treatment should be used in any event. It has been used on our work sometimes by mistake but without any distinct results one way or another so far as is known.

The matter of protective coatings for marine structures is one of the most confusing and complicated subjects we have to face. In fact, this is a subject on which one never gets a completely satisfactory answer at any time and the reason for this is that basic conditions are never the same on any two jobs. When this is considered along with the climatic conditions referred to previously and with the factor of personalities, such combinations of conditions occur that almost anything can happen at any time and frequently it does. In this connection it is continuously surprising that condition combinations which seem to clearly indicate a certain result will suddenly turn up something quite different.

Because of this it is not proposed to try and describe in too much detail about coatings except to say that BuDocks has tested literally thousands of them and unfortunately a great proportion of them have not done what was claimed for them. This accounts for a previous reference to over-enthusiastic salesmen or scientists and the dangers which might flow from too close an adherence at times to their recommendations. On the other hand, all these trials and experiments have resulted in some really good coatings which meet requirements to an extent which seems reasonable. Full information on coatings used over the years is available to anyone interested. Search is still being made for the "end of all trouble" coatings, however, and the study and help of the delegates here are still needed.

The subject of coatings should not be left without pointing out the need for further study and experiments on methods of application. Many coatings can be brushed or sprayed and wherever the latter method can be safely applied, great economies are possible. With heavy coatings like the hot and cold coal tar base ones which incidentally are among the very best, however, spray application is still in a rather experimental stage and if anything can be done to further the development of such methods of application it will be most helpful.

Significant of efforts to maintain our steel water front structures at this time are experiments and trial runs with self-applying coatings and cathodic protection. Both of these methods are only practicable in the particular field of floating dry docks in their possible application to parts of the structures which are in the water all or most of the time. From this point of view, it is suggested that cathodic protection is somewhat more limited in its possibilities.

Self-applying coatings refers to materials which are poured on the surfaces of enclosed areas such as a ballast tank of a floating dry dock or derrick pontoon. The expected action here is that the material will float on the surface of the contained water and attach itself to the exposed surfaces of bulkheads, structural members, etc. by the action of the water going up and down due to pumping or flooding or to the structure's changing its position otherwise, i.e., listing and trimming. Surfaces to be treated with these materials do not have to be cleaned down thoroughly but, of course, some cleaning of the worst rust and debris deposits will facilitate the finally desired action. When attached to the surface in question, the material is supposed to first soften up and remove existing rust and then continue to coat the clean surfaces so that no further rusting will occur. As with every new protective method used or experimented with, this method has its good and bad points. In the first place, the material is not cheap. It costs about $50,000 to $60,000 to start off an 18,000 ton dock and, of course, it costs something for additions to keep the coating going, probably about 10% of the original cost per year. It is also possible, as unhappy experience shows, to pump the solution overboard with the ballast water if care is not used in pumping operations. The solution is also blown out of the vent stacks in filling operations on some type docks and attempts have been made to develop baffles to stop this action. Finally, the material does not protect the lower 18" or so of the tanks. The overhead surfaces are also a problem but some effect is obtained here by occasionally listing the structure being protected. Experience on this type of material has been gained by using it experimentally in a rather large way of necessity and some encouraging results are beginning to appear. It is still considered an experimental coating, however, it is hoped that it will be successful, but bitter past experience forces a skeptical outlook. The composition of this coating is not available because it is a proprietary compound. Some of the ingredients are know, however, like pine oil and lanolin because the manufacturers ask for help in obtaining them inasmuch as they are on the critical list. There is hope of soon developing at least

a performance specification for this material and the three manufacturers available will then give some real competition and it is hoped with consequent reduction in cost.

As for cathodic protection, in the author's own field, it is emphasized here also that this is an experimental field. There have been some strong efforts lately by enthusiasts to try and convince maintenance engineers that cathodic protection is a complete method. This is definitely not true. Cathodic protection has its uses and for some conditions it is definitely good. For instance, on the 120-mile water supply line running from Florida City to Key West, Florida, it has been successful in helping to combat leaks, but in a large sense otherwise and elsewhere it has yet to definitely prove itself. The present status of the Bureau's work along this line as regards floating dry docks is briefly as follows:

The Bureau has under way two test installations on cathodic protection of floating dry docks. One of these is installed on the AFDL-12 at Long Beach. This is an inactive dock and the cathodic protection is on the exterior of the hull only. The system used is the graphite anode-impressed current type and reports to date indicate that satisfactory protection is being obtained. This dock was newly scraped and painted just before installation of the cathodic protection system. This installation has been in operation about 15 months. The other installation is on the AFDL-28, an active dock at Key West. This also is the graphite anode-impressed current system and installation has been made on the exterior hull and the interior ballast compartments. One report has been received to date and it indicates that the exterior installation is satisfactory and adequate protection is being obtained, but the interior installation is not satisfactory as of this time and the protection being obtained is not adequate. It appears that the inadequacy of the interior protection is due at least in part to a poor arrangement of the anodes. The systems on this dock have been in operation for about 9 months. This dock also had been newly painted just prior to installation of the cathodic protection system. No test installations have yet been made, making use of magnesium anodes, chiefly because satisfactory arrangements have not yet been completed with the magnesium people.

As for other cooperating groups, the Bureau of Ships is making test installation on some of their ships, both active and inactive, and their experience has been in general about the same as that of the Bureau.

The Maritime Commission has had test installations of both the graphite and magnesium systems on their ships for several years and it is understood that they feel that the protection being obtained is adequate. However, it is understood that this is based upon the potential readings which are taken from time to time and is not based upon actual observations by docking ships after the installation has been in effect for several months.

The Canadian Navy has been studying cathodic protection for several years

and from their reports, they appear to be convinced that it furnishes adequate protection against corrosion. These reports have mentioned actual observations made when the ships have been docked after the installation has been in effect for some time. The Canadians are also trying this type of protection on active operated ships as well as their inactive vessels.

Some of the questions which still remain to be answered on cathodic protection insofar as we are concerned, are the following:

A. What is the effect of fouling upon cathodic protection? Will a cathodic protection installation on a badly fouled hull protect that hull? It would seem reasonable to suppose that heavily fouled hulls would retard or possibly make non-effective the cathodic protection system.

b. Over protection is harmful in that if too much current is applied, the paint coating is adversely affected. Present thought on the use of cathodic protection is that it would be an adjunct to painting and if effective, would lengthen the time between dockings. It has not been considered a complete substitute for painting. It is understood that this is also the viewpoint of the Bureau of Ships. It could be that the Maritime Commission feels that they cannot affort both docking for painting and cathodic protection and therefore, are using the cathodic protection systems as an alternative method for painting.

c. From the Bureau's experience and also from talking with other people, it appears that cathodic protection is not effective at the water-line area. Painting would, therefore, be required at this area whether or not cathodic protection is used and for an active operating dock, the water-line area would extend from light draft without a ship in dock to the pontoon deck level.

From the Bureau's experience it is confidently believed that cathodic protection has good possibilities for the portion of the dock that is always under water but enough is not yet known about its effectiveness to warrant 100% reliance upon it and it is not felt personally that it will ever be the answer to all of exterior underwater corrosion problems.

The deterioration of concrete structures offers somewhat the same problems as with steel structures in that there is sometimes trouble with structures at or near the water front which are not submerged in sea water. The reference here is to conditions such as recently experienced in Bermuda and the West Indies in particular where serious concrete disintegration problems occurred due to the direct action of salt water which it was sometimes necessary to use in mixing concrete or to the action on the concrete of salt-laden spray. In both cases, the effect of the salt water was aided and abetted in its action on the reinforcing steel and conduits by the fact that available aggregates were somewhat porous in nature.

Where trouble occurred from this source it was necessary to do some patchwork on the concrete, clean off all the old paint if any, then apply some kind of a coating such as an asphalt aluminum paint to seal the pores of the concrete. In cases where anticipated trouble has not yet been experienced a richer concrete mix is used to clean the coarse aggregate of its loose and chalky coating and wash it in fresh water. Also where possible, reinforcing steel is cleaned of heavy rust and dipped in a cement slurry before being placed. In general, in areas like this resort is made also to un-reinforced concrete wherever possible and placing electric conduits in the concrete is avoided.

By far the most of our trouble here, however, is with structures in direct contact with the salt water. Even so, great advances have been made over the troubles of the early twenties when engineers labored under that misguiding slogan of "concrete for permanence" and did not generally know what is known today about how to design, mix and place concrete for long-term results. During the period mentioned a regular plethora of concrete water front structure failures occurred and it seems now on looking back on that period, that a large part of the work was major repairs to such structures due to the action of sea water on the cement and the reinforcement. Experiences here resulted in the Bureau's present very fine standard specifications for concrete work. When the standards laid down in these specifications are adhered to, good dense, durable water front structures are possible anywhere in the world. There still are troubles, however, but they are mostly very special troubles. Examples of these special troubles are the growth or swelling of large mass poured tremie concrete structures such as the Bureau's two major graving docks at New York which have increased in length in one case by about 10 inches since they were completed about 6 or 7 years ago. Elaborate studies have been made of this condition to determine its cause if possible and what the effects of this growth are on the strength and usability of the structures. The studies here have run into dead ends on all counts and nothing has been found to account for the growth. Numerous borings were made and all indicated satisfactory strength and normal chemical characteristics. Also reinforcing and form steel where exposed, showed no rusting even in one suspect location where a trench was opened in the dock floor nearly to the bottom of the dock. Different cements and aggregates were used on this work of necessity at times and samples of similar materials, when analyzed, gave us no clues to explore further. Here is a problem which may or may not be serious later although there is no indication now that it will be.

In a somewhat similar dock at Newport News, this same general problem occurs and it is already definitely serious. In this case, marsh gas is formed in the underlying materials and this works its way up through the seasoning cracks in the concrete mass and by crystalline action is causing the concrete abutment to swell and crack. No practicable solution has been found to this problem either and therefore, the possibility is faced that the abutment will have to be rebuilt in say 25 to 30 years. On this particular problem Terzagli was consulted by the Yard operator and it is understood that he is still studying the problem. Other tremie concrete struc-

structures built about the same time as the two mentioned have given no particular worries. That doesn't mean, however, that they will not give trouble as time goes on and it is believed that all these structures should be carefully watched for some years to come and a special inspection has been instituted in regard to them that will do just that. Concrete hulls for other structures such as floating dry docks and barges of which the Bureau has a considerable number have in general given remarkably little trouble in a period of about seven years of active service and as regards them, a statement made previously in this talk is again made, namely, that if our water front structures are built in strict accordance with our latest concrete standards they will be good structures. Hull maintenance costs on these concrete floating structures in comparison with steel are very low, possibly in the order of 20%. For this reason, in new designs for such structures, the Bureau is going just as far as possible in the use of concrete.

In these new studies of the use of concrete for floating structures concrete is being given every possible break in the way of taking advantage of the possibilities of precasting and prestressing the concrete, decreasing coverage for reinforcing steel, using mesh reinforcement in lieu of bars, etc. This is all design, however, which should be left to others on the program but it is mentioned because it has to do with possible later deterioration problem. At the end of the war, two experimental concrete barges were constructed, one largely of precast concrete box construction and one of prestressed concrete construction. These barges have now been in constant normal water front use for a period of about seven years and both have been satisfactory, and maintenance costs on them have been very low. It is significant to note here that the prestressed concrete one which might be expected to have a minimum of cracks, has the greater number of cracks and there is some indication that some prestressed elements or areas are no longer in the original condition. If this is the case, prestressed concrete loses a lot of its appeal from the maintenance point of view because the main thing sought in such construction was more insurance against salt water attack on reinforcing steel and other embedded metals. In the present state of the art of prestressing in this country, claimed economies from prestressed concrete are considered decidedly futuristic.

Many more things could be touched on in a talk like this if time allowed. It is thought, however, that the best way to follow up the points mentioned as needing further study is by conferences, exchange of data and perhaps sometimes by correspondence. The Bureau is always glad to share in these activities as prèviously indicated, and delegates are invited to follow up particular interests with the Bureau at this present meeting or at any future time.

(Contribution from The International Nickel Company, Inc.)

CORROSION AND PROTECTION OF STEEL IN SHORE LINE AND OFFSHORE STRUCTURES

by F. L. LaQue

This discussion of corrosion of steel is offered as a supplement to the many other papers presented at this Conference which are concerned primarily with the action of marine organisms on timbers. For many purposes, steel has structural advantages over timber and, for some of these, it is the only good choice. Its principal disadvantage is its susceptibility to corrosion which, unless arrested by appropriate means, can occur at rates that will destroy the structure well before the desired life has been reached. It is appropriate, therefore, that some attention be given this subject at this Conference.

From measurements on test piles installed at Kure Beach, N. C. over a period of several years a typical profile of corrosion in clean sea water has been established[1]. Maximum attack occurs in the wave splash region just above high tide level. Here it is about five times as great as underwater and about twice that in the atmosphere above the splash zone. Minimum attack occurs towards the bottom of the tidal zone where it is from one-half to three-quarters that well below low tide. This distribution of attack has been confirmed by similar measurements on piles withdrawn from actual installations.

The greatest variation in rates of attack are observed at the mud line, in the splash zone and above it and, to a lesser extent, within the tidal range.

It will facilitate discussion to consider each of the five zones of attack separately:

Zone 1 - Below the Mud Line

As compared with attack in some of the other zones, that below the mud line is not likely to occur at a serious rate. Ordinarily, the rate of corrosion will not exceed that in the water below low tide. In some instances, as where sulfate reducing bacteria are present to stimulate corrosion, there may be accelerated attack at and just below the mud line. The steel in this region may become anodic to the steel in the water and, thereby suffer extra damage to the extent of two to three times that which occurs in the waterand elsewhere in the mud. The area affected is somewhat uncertain, but ordinarily will not extend more than a couple of feet below the mud line where the location of this remains substantially fixed. Where there is cyclic building up and washing away of mud from around the bottoms of piles, the area affected will vary accordingly. Where no other

[1] H. A. Humble, "The Cathodic Protection of Steel Piling in Sea Water," Corrosion, Vol. 5, No. 9, September 1949.

remedial measures are to be used, this extra corrosion just below the mud line may be provided for by applying pads of extra metal before driving the piles if the ultimate location of the mud line can be determined accurately enough in advance. Otherwise, it may be possible to install reinforcing shields or collars after the piles have been driven. The actual need for these steps will be difficult to determine in advance unless there is some direct experience with other steel piles in the same locality to serve as a guide.

The most effective way to prevent corrosion underground will be the application of cathodic protection, preferably as a supplement to an organic coating which will be helpful in reducing the current requirements and achieving distribution of the protective current throughout the buried length of the pile. Coal tar enamels and vinyl coatings represent good choices of coating for this purpose. Since cathodic protection of the underground surfaces will always be associated with cathodic protection of the underwater surfaces, the current requirements will be established for the combined areas and it seems safe to assume that the criteria of protection used for the underwater areas will automatically include the underground surfaces as well.

Zone 2 - At the Mud Line

In addition to the accelerated attack in the region just below the mud line already discussed, there may be very severe erosion at the mud line itself. This will occur on piles driven in shallow water on a beach where the action of the waves will cause severe scouring by sand held in suspension. This may proceed at rates of thinning as high as 0.05 inch per year from each surface exposed to the scouring action. Such rates have been observed on sheet steel piling in the jetties at Kure Beach and in certain groins at Palm Beach as described by C. W. Ross[1] of the Beach Erosion Board.

Although this attack probably involves considerable corrosion of surfaces freshly exposed by abrasion, there is so much simple mechanical wearing away that it seems unlikely that cathodic protection would prevent this scouring action. Nor are ordinary protective coatings likely to survive long enough to be effective. Wooden and concrete shields have been used with spotty success. Wood, of course, would have to be treated with preservatives against marine borers. Concrete is subject to cracking and spalling - especially if corrosion of the underlying steel is not arrested completely.

Experience with piles in such a location as described by Kartinen[2] of the Signal Oil & Gas Company demonstrated an amazing effect of the shape of the pile in reducing mud line erosion. The wasting of a tubular section was found to be only a small fraction of that of conventional 'H' pile

[1] C. W. Ross, "Deterioration of Steel Sheet Pile Groins at Palm Beach, Florida," CORROSION, Vol. 5, 1949, p. 339.

[2] E. Kartinen, "Discussion at Sea Horse Institute Informal Conferences, 1951-52.

sections. It was found to be practical to protect 'H' piles effectively simply by encasing them in tubular shields in the mud line region. Where heavy 'H' pile sections were eroded through in less than 20 years, tubular shields only 3/16 inch thick were able to survive. In the practical installation the space between the tubular shields and the 'H' piles was filled with concrete grouting. In some instances, also, tubular piling was given satisfactory protection by a silica sand reinforced somastic coating which also exhibited good resistance to sand scouring.

Since the steel in the tubular shields was inherently no more resistant to erosion than the steel in the 'H' piles, the better performance of the tubes must have been due primarily to their more favorable shape. Evidently, the pattern of flow of water and suspended sand around a smooth cylinder is accompanied by much less severe erosive forces than are associated with the impact of currents and eddies on the 'H' pile shape.

This suggests that this favorable property of tubular piles should be given considerable weight in choosing such a shape rather than an 'H' section for piles to be driven where sand scouring may be anticipated. It seems likely also that the tubular shape would have an additional mechanical advantage because of the lower stresses resulting from the lesser impact of waves.

In any event, in the light of these experiences, it would be well to provide 'H' piles with tubular shields to prevent excessive wastage by sand scouring where this may be expected to occur.

Zone 3 - Below Low Tide

Corrosion below low tide is not likely to be a major factor in determining the life of a steel pile. As measured by weight loss, the rate of attack is not likely to exceed 0.005 inch per year - local attack by pitting may reach a maximum of three times this rate over an extended period. In tropical waters where calcareous deposits are likely to coat the steel, even lower rates of attack may be anticipated.

When some steel piles were being removed from an offshore structure on the Pacific Coast recently E. Kartinen of the Signal Oil & Gas Company observed very peculiar and severe corrosion of surfaces near the bottom. This took the form of keep hemispherical pockets, each of which was occupied by a living sea urchin of the species Strongylocentrotus purpuratus. The surface of the steel below these organisms was bright as though it had been suffering continuous active corrosion, possibly as a result of the action of the sea urchin in keeping the metal abraded slightly so that no protective corrosion product films could develop. Presumably this would require the activity of a series of successive inhabitants of the pockets with the size of the occupying organism increasing with size of the pocket. Apparently this association of sea urchins with corrosion is rare, since there are no previous reports of similar occurrences on record.

Corrosion under water is not difficult to control by cathodic protection by itself or as a supplement to an organic coating such as coal tar enamel or a vinyl system. For bare steel a current density of 3 milliamperes per square foot should suffice. In time, this can be reduced gradually, perhaps to as little as 1 milliampere per square foot. A useful criterion of protection is the measurement of the potential of the pile with reference to a saturated calomel half cell. When the steel has been polarized to a potential of 0.8 volt or higher, it may be assumed that corrosion has been practically arrested. The applied current can be adjusted on this basis.

A rugged pure zinc electrode may be substituted for the fragile calomel half cell for potential measurements. With zinc as the reference, the potential of the pile should be held not more than 0.2 volt more noble than the zinc.

When supplementary organic coatings are used, the current requirements are reduced considerably - to an extent determined by the permeability of the coating, the number of holidays in it originally and the number of bare spots that develop during pile driving and in service as a result of accidental damage or effects of marine organisms. Organic coatings may also be damaged by the application of too much current for protection and the consequent generation of excessive alkali, and especially hydrogen which may blister the coatings severely[1]. This form of coating deterioration may be avoided by restricting the applied current so that the polarized potential of the steel will be held close to the desired 0.8 volt vs. calomel and not in excess of 0.9 volt.

In some instances it has been recommended that the cathodic protection of steel in sea water should be made completely effective immediately by the short time (one to two weeks) application of current at a high current density, e.g. 50 to 100 milliamperes per square foot[2]. This will serve to lay down a protective calcareous coating and, when this has been formed, protection may be maintained with the much lower current density of 3 milliamperes per square foot or less previously mentioned. In view of the possibility of damaging organic coatings by excessive current, it would seem that the initial use of high current densities should be restricted to bare steel surfaces. Where coatings are used, also, the current should be controlled to the amount required to polarize the steel to the desired level of potential.

[1]A. J. Eickhoff and D. L. Hawke, "Some Factors Affecting Paint Performance on Cathodically Protected Steel," CORROSION, Vol. 7, 1951, p. 70.
L. P. Sudrabin, F. J. Lefebvre, D. L. Hawke and A. J. Pickhoff, "Some Effects of Cathodic Protection on Conventional Paints," CORROSION, Vol. 8, 1952, p. 109.
R. P. Devoluy, "Coating Experiences with Cathodic Protection Underwater," Paper presented at NACE Meeting, Galveston, March, 1952.

[2]See C. C. Cox, U. S. Patents 2,200,469 (1940) and 2,417,064 (1947) and British Patent No. 540,487 (1941).

Magnesium anodes are a convenient source of current for cathodic protection in sea water. Otherwise, current may be furnished from some external source, such as a rectifier and applied through more or less permanent graphite on expendable steel anodes.

Additional details concerning cathodic protection of steel in sea water may be found in papers by H. A. Humble[1] and a description of a practical installation on an offshore drilling structure in a paper by E. Doremus and G. Doremus[2].

An idea of the current required for protection in connection with organic coatings may be obtained from the data in Table 1 which shows the current density required to maintain piles covered with different coatings above the protective potential after about 2 years at the Harbor Island Marine Test Station.

Zone 4 - Tidal Zone

Contrary to popular belief, corrosion does not reach a maximum in the tidal zone. In fact, minimum attack may occur here near the bottom of the usual tidal range.

An explanation for this has been found to lie in a powerful differential aeration cell which becomes established each time the tide comes in. The frequent and better access of air to the surfaces between tides causes the water in contact with them to be higher in dissolved oxygen than the water that seeps through the layer of rust and marine organisms on the under water surfaces. This makes the tidal surfaces more noble than the underwater surfaces and, therefore, the protected cathodes of the cell that is developed. The measured distribution of potential in a particular case showed the top of the tidal zone to be 90 mv. more noble than the steel under low tide.

The effect of these local action currents on corrosion in the tidal zone was demonstrated[3] by the difference in corrosion of continuous as against isolated specimens of steel disposed through the zones of interest. Isolated specimens in the tidal zone were corroded ten times as much as companion portions of a continuous plate which passed through this zone into the water below low tide.

[1] H. A. Humble, "Cathodic Protection of Steel in Sea Water with Magnesium Anodes," CORROSION, Vol. 4, 1948, p. 358.
H. A. Humble, "The Cathodic Protection of Steel Piling in Sea Water," CORROSION, Vol 5, 1949, p. 292.

[2] E. P. and G. L. Doremus, "Cathodic Protection of Fourteen Offshore Drilling Platforms," CORROSION, Vol. 6, 1950, p. 216.

[3] F. L. LaQue, Marburg Lecture "Corrosion Testing," Proceedings Am. Soc. Test. Mat., Vol. 51, 1951.

TABLE 1

CURRENT DENSITIES REQUIRED FOR CATHODIC PROTECTION
OF PILING AT HARBOR ISLAND 1950-51

Type of Pile	Type of Coating	Current Required to Polarize* to 800 to 850 Millivolts vs. Calomel Half Cell - Ma. Per Sq. Ft. After 2 Months	After 11 Months
H Beam	None	1.6 to 2.4	1.2 to 1.8
Tubular	None	5.9	3.3
I Beam	Coal Tar Enamel Above Low Tide	2.0 to 2.8	1.2 to 3.4
Tubular	Coal Tar Enamel	0.02 to 0.04	0.06 to 0.18
H Beam	Coal Tar Enamel	0.17	0.13
H Beam	Vinyl System	0.15 to 0.33	0.33 to 1.1
H Beam [1]	Tnemec	0.44	1.8
H Beam [1]	Insulmastic	0.26	0.31
H Beam	Monel Sheathing Above Low Tide	1.6 to 2.1	1.6 to 1.7
Tubular [1]	Monel Sheathing Above Low Tide	2.6 to 2.7	0.8 to 1.5
Tubular [1]	Nickel Sheathing Above Low Tide	0.7	1.4
H Beam	70:30 Cu Ni Above Low Tide	0.07	1.0

*All piling polarized initially at 40 ma./sq.ft. for 2 months
[1] Piles in area where sea water is under constant agitation.

These data not only account for the peculiar distribution of corrosion but point to the necessity of using specimens large enough to extend through the zones of interest in studying corrosion and protection of steel piling. The exposure of small specimens below low tide and between tides will not give the proper answers.

In some harbors, also, corrosion in the tidal zone may be reduced by the protective effect of oil and grease films deposited on the metal by falling tides where the surface of the water is regularly covered with oil.

From the standpoint of protection, the tidal zone presents a difficult problem. Cathodic protection cannot be depended upon to extend much above half tide level except where the tidal range is so small relative to the common height of waves that the whole tidal range is kept submerged most of the time.

Organic coatings, such as coal tar enamels and vinyl systems are effective for a time, but it seems unlikely that they would survive for the desired life of the structure and their replacement involves many practical difficulties. Chief among these is the proper preparation of the surfaces to receive new coatings during the short time between tides that these surfaces can be kept dry - especially if there is any wave action or spray to contend with. The soft coal tar enamels are also subject to penetration by barnacles which can embed themselves in the enamel and eventually expose the underlying steel. Developments are underway to reinforce such enamels against barnacle penetration by the incorporation of sand or the application of cement slurries. These steps may suffice to avoid this form of deterioration of enamels.

The inadequacy of organic coatings and cathodic protection for long time prevention of corrosion in the tidal zone has led to interest in metallic coatings for these regions.

Protective metal sheathing may be applied in the form of rolled sheet metal made to conform to the shape of the piling. This is obviously easiest with tubular piles, more difficult with structural shapes, such as 'H' pile sections, and very difficult with interlocking sheet piles where covering the knuckles would require butt straps and a complicated method of sealing the lower end of the sheathing to keep water from rising and falling along the knuckles and under the butt straps. 'H' piles may be sheathed with conforming shapes or the sheathing may be wrapped around. The latter practice requires that the lower ends of the sheathing be supplemented by a previously formed metal box which can be inserted to fill the space between the sheathing and the web. When this has been accomplished, the space between the sheathing and the web can be filled with sea water to which caustic soda has been added to raise the pH to 11.5. This requires about 4 ounces of NaOH per cubic foot of sea water. The air free alkaline sea water prepared in this way is not harmfully corrosive to steel under the conditions that exist inside the sheathing: the rate of corrosion observed in a particular test was only 0.0002 ipy.

In the case of conforming sheathing, it is possible to seal the joints at the top and bottom by welding. However, there is a question as to whether this sealing is actually required. It would be expected that even if these joints were left open the first water to seep between the sheathing and the steel would soon form sufficient rust to occupy the space and thus prevent access of any additional water or oxygen to cause further corrosion. The danger of corrosion here can be reduced considerably by applying a coat of coal tar enamel to the piling or the sheathing just before the latter is applied and without letting the coating dry before the sheathing is put into place.

Some tubular piles have been sheathed experimentally with light gauge Monel sheets held in place only by Monel bands applied in the same manner as box strapping. Other Monel sheaths have been applied by the use of wire bands.

Monel is a logical choice for this sheathing because it demonstrates excellent resistance to corrosion under these conditions of exposure. Monel sheathing has been applied to tubular sections in offshore drilling structures[1]. The presence of numerous cross braces in the region to which the sheathing had to be applied complicated this operation. For this reason, it would be desirable, if at all possible, to design braced structures so that the bracing would either be below half tide level where it could be protected by cathodic currents, or above the splash zone where paints could be applied readily.

It has been discovered that the cathodic polarization characteristics of Monel as compared with steel in the tidal zone are such that the cathodic protection of the associated steel is accomplished more readily with Monel in the tidal zone than if the tidal zone were left as bare steel. Measurements of the galvanic current between steel below low tide and Monel in the tidal zone as compared with steel below low tide and steel in the tidal zone have shown less galvanic effect of the Monel than the differential aeration cell effect between steel and steel.

In applying Monel sheathing in connection with cathodic protection as is recommended, the sheathing should start at about half tide level and extend through the splash zone where the periodic renewal of organic coatings would be very difficult, if not impractical.

Some attention is being given the use of metal protection in the form of sprayed metal coatings applied to previously sandblasted surfaces. Of the two metals proposed for this service, zinc seems to be preferred over aluminum. The applied thickness should be from 10 to 15 mils and the sprayed metal should be supplemented by a plastic sealer in the form of a chlorinated rubber vehicle carrying a very small amount of pigment. Presumably the sprayed metal need be applied only above half tide level, since cathodic protection will take care of the lower surfaces.

[1]F. L. LaQue, "Protection of Steel in Off-Shore Structures," DRILLING, June 1950.

Zone 5 - Splash Zone

The splash zone is where the greatest attack will occur unless protective measures are taken. The extent of corrosion in this zone may vary through wide limits, depending on the locality. Attack will be greatest where there is considerable wave action, and especially where breakers kick up a great deal of corrosive spray. By and large, the means of protection proposed for the tidal zone will also be best for the splash zone and for the same reasons. The principal difference will be that penetration of soft coatings, such as coal tar enamels, by barnacles will not be a problem.

Practical tests, especially on offshore drilling structures[1], have shown that vinyl systems have particular merit for this service. The steel surfaces must be prepared carefully by sandblasting and the metal must be dry when painted. The first coat should preferably be a washcoat primer plus successive coats of vinyl paint so as to yield a total paint film thickness of at least 6 mils. The common pigments, such as red lead, zinc chromate and iron oxide, have performed satisfactorily with the inhibitive pigments being preferred at least for the first coat over the washcoat primer.

Aluminum may be used as well as zinc as a sprayed coating above high tide level. The thickness of either metal should be about 0.008 inch and the metal spray should be supplemented by a coat of primer and two top coats of aluminum flake in a vinyl vehicle.

Composition of Steel

The composition of the steel used will have no great effect on corrosion or the facility of protection in the mud and up to half tide level. However, by suitable alloying, it is possible to effect considerable improvement in the resistance of steel to corrosion in the upper part of the tidal zone, and especially in the splash zone and above. The possible extent of this improvement in corrosion resistance is indicated by results of tests of steels exposed near the breakers at Kure Beach where the rate of corrosion of a 5% nickel steel was only 1/20 that of steel which contained only 0.01% copper. It is not suggested that steel for this service should contain as much as 5% nickel - these data are included merely to illustrate the extent of improvement that is possible. Research is currently underway with the object of developing steels of much lower alloy content, e.g. 0.5% - total made up of a combination of such elements as nickel, copper and phosphorus which show promise of effecting considerable improvement in corrosion resistance with only a small increase in cost of steel. While this property will increase the life of the steel without supplementary protection, it will be of particular value in increasing the durability of organic coatings which can be expected to show improved performance on the more corrosion resistant steels.

[1] W. M. Thornton and M. L. Bilhartz, "Protection of Offshore Production Equipment" - Paper presented at NACR Meeting, Galveston, March 1952.

Reinforced Concrete and Concrete Protection

Before closing this discussion, some remarks re the use of concrete are in order.

Assuming a proper mix of concrete and adequate coverage of the steel, there should be little deterioration of concrete below low tide level. A proper mix of concrete based on requirements for the most severe exposure in the tidal zone may be defined as one made up to contain not less than 7 sacks of cement per cubic yard of concrete with a maximum total water content of 5 gallons per sack of cement carefully measured as recommended by the Portland Cement Association.

In waters where marine borers of the pholad types may be encountered, the use of hard silica sand to form a concrete of high strength, e.g. 4,000 pound minimum test, will be required to resist penetration and deterioration of the concrete by these borers.

There is some controversy as to the minimum thickness of coverage of concrete over the steel. The most conservative recommend a minimum of 3", with 4" at corners. Others believe that with the best grades of concrete properly applied the coverage can be reduced to 2". Apparently, there is greater latitude with respect to coverage and grade of concrete for those surfaces that are always under water. Requirements become more stringent in the tidal and splash zones where the concrete is alternately wet and dry. Here the chance of deterioration of the concrete and penetration of water to corrode the steel is greatest. If any appreciable corrosion occurs, the accumulated corrosion products will induce cracking and spalling of the concrete and deterioration will proceed at an accelerated rate. Even with good grades of concrete there are difficulties due to spalling and cracking in northern climates where the concrete is subject to wide fluctuations in temperature, with freezing during the winter months.

Attention is being given the application of cathodic protection to the steel reinforced concrete. However, such protection is likely to be effective only below low tide where it apparently is least required. There is a considerable question as to the benefits to be gained from cathodic protection of reinforced concrete in the most critical tidal and splash zones. In addition, there have been reports of deterioration of the concrete when the applied current or voltage have been too high. Several years ago, the National Bureau of Standards observed weakening of the bond between the concrete and the reinforcing steel when current was applied to the steel as a cathode on specimens immersed in Washington, D. C. tap water[1].

Protection of Steel Hardware and Fittings

Steel in such forms as bolts, tie-rods and the like is used frequently in the assembly of timber structures. It is desirable to give such steel

[1]E. B., M. McCollum, and O. S. Peters, Technologic Paper #18, "Electrolysis in Concrete," National Bureau of Standards, 1919.

parts some protection, as by the application of organic coatings, such as coal tar enamels, or metallic coatings, such as zinc. Cadmium has also been used in place of zinc and there has been some controversy as to the relative merits of zinc and cadmium for protecting steel in marine atmospheres.

Results of tests in progress at Kure Beach show a considerable advantage of cadmium over zinc. Specimens carrying different thicknesses of electro-deposited coatings have been exposed to the sea spray atmosphere near the breakers. The dataassembled in Table 2 indicate the greater durability of the cadmium coatings and the advantage of using coatings of adequate thickness, especially in the case of zinc.

Some interest has been shown also in the use of Monel for fastenings in this service. Tests indicate that such Monel fastenings will have an extremely long life.

TABLE 2

PROGRESS OF RUSTING OF ZINC AND CADMIUM PLATED STEEL SPECIMENS EXPOSED TO SEA SPRAY ATMOSPHERE AT KURE BEACH, N. C.

Coating Thickness Inch	Percentage of Rust after									
	58 days		176 days		364 days		483 days		514 days	
	Zn	Cd	Zn	Cd	Zn	Cd	Zn	Cd	Zn	Cd
0.000050	100	60	100	80	100	100	100	100	100	100
0.000100	95	1	100	10	100	60	100	83	100	87
0.000200	1	/1	5	5	68	9	100	17	100	20
0.000500	0	0	0	0	2	0	2	/1	6	2
0.001000	0	0	0	0	1	0	1	/1	1	/1
0.002000	0	0	0	0	1	0	1	/1	1	/1

(Contribution from the U. S. Army Engineers and the Department of Agriculture)

SPECIAL PROBLEMS OF DETERIORATION IN ARMY WATERFRONT STRUCTURES

by J. A. Beal, R. J. Kowal, W. D. Reed

INTRODUCTION

During recent years there has been an increased interest in the deterioration of wood and wood products and particularly in the damage caused to buildings. This has been due, to a considerable extent, to the increasing values of properties and the high cost of their maintenance. Costs for some grades of lumber and structural timber have increased approximately 200% since 1942.

There have been other reasons for this interest, however. The wide use of second-growth timber as a structural wood has resulted in losses greater than heretofore known, due to insect damage, decay, and other forms of deterioration. Such woods, particularly second-growth southern pines, contain little heartwood and a considerable volume of sapwood which lacks resistance to deterioration.

Changes in style of building construction have also created conditions favorable to insects. The practice of erecting structures upon concrete slabs, for example, favors termite activity, and the use of heating systems in cold climates has had a marked influence--large central heating and humidifying units serving to create conditions, even in the substructure of buildings, that enable insects to continue their destructive activities throughout the entire year rather than on a seasonal schedule as they would normally do.

Estimates of current losses due to such organisms as subterranean and non-subterranean termites, wood borers, powder-post beetles, marine borers, and decay, are astounding. In the Canal Zone alone, the Corps of Engineers was until recently spending almost $500,000 annually for repairs to buildings damaged by subterranean termites; establishment of an effective termite control program has reduced these losses greatly. Losses caused by non-subterranean termites, although not so great, are very high also, particularly in the semi-tropics and tropics. In certain areas, such as the Florida Keys and the West Coast, they are far more severe than subterranean forms. There are a large number of wood-boring insects which in the aggregate annually destroy finished products valued at several million dollars. Accurate estimates of these losses are unavailable due mainly to the fact that because of the insidious nature of the insects' activities, they have attracted less attention, and as a result have been less intensively investigated.

In recent years revolutionary advances in the field of pest control, particularly in the development of synthetic organic insecticides and the equipment for applying them, have opened possibilities for insect control never before realized. The value of these new chemicals should be tested for the protection of wood by surface treatments, soakage, and the use of the pressure-vacuum process.

In the discussion that follows, it should be kept in mind that the various groups of insects mentioned, as well as the wood-rotting fungi, reach their optimum development under conditions existing in shore environments. This is due mainly to the high relative humidity and heavy rainfall occurring in such areas, and in warm climates to the prevalence of high temperatures.

A brief discussion follows on the various groups of organisms and the nature of their habits, distribution, and the destruction they cause.

Termites

Termites are the most destructive of all woodboring insects attacking wood structures, Distributed the world over, they have attracted a great deal of attention and study by both scientist and layman. Thus, there is a wealth of literature surrounding these interesting forms, some of it truly scientific, but much of it erroneous and bordering on the fantastic.

For many years termites were known as white ants, a misleading nomenclature which persists to this day. Actually, they are not even remotely related to ants nor are they necessarily white. Rather, they are a primitive group of insects, related to the cockroach, and comprise a distinct order of their own. However, like ants, they are social insects living in large colonies organized in a caste system, the castes usually consisting of winged adults and wingless soldiers and workers.

Although there are innumerable species of termites with wide variations in character and habit, only two general types need be considered from an economic viewpoint-- namely, the subterranean and drywood termites.

Subterranean termites are so called because of their habit of maintaining the center of their activities, the colony, below the soil. The castes normally consist of dark-colored winged adults and soft-bodied, white or cream-colored soldiers and workers. The normal activity of termites of economic importance is that of consuming and decomposing cellulose materials, such as dying and dead plant life, back into organic constituents of the soil. However, if they are deprived of this and buildings occupy the site, the termites are capable of infesting the structures either by direct entry into readily accessible structural wood, or, if the wood is some distance away, by means of earthen shelter tubes built over obstructions. Thus, by means of these humidified and ventilated tubes, termites can progress from their colony deep in the earth over brick, concrete, or masonry, or through tiny cracks in these units, and even over treated wood, until they reach the untreated wood or other cellulose products they desire. While they normally confine their activities to wood in the foundation structure, it is not unusual for these insects to extend their activities into the second

or third story in order to reach suitable food, this being particularly true in shore areas, where high humidities prevail.

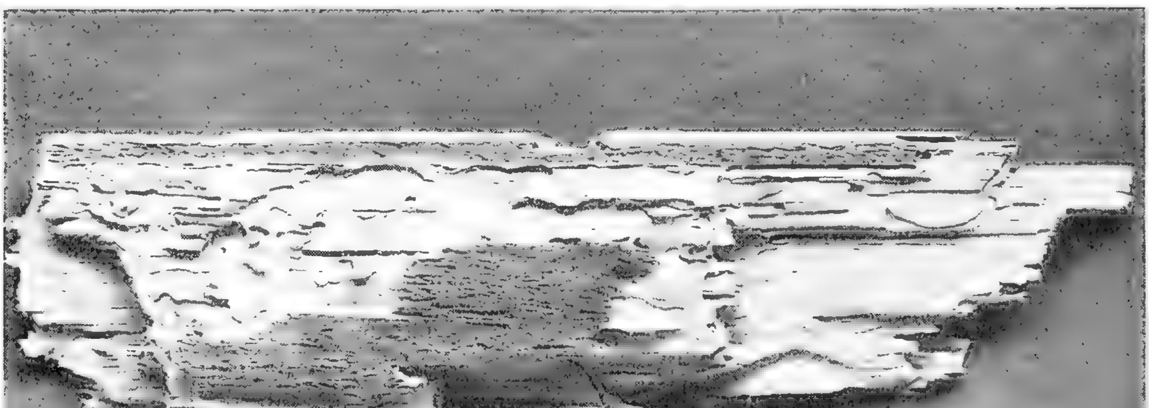
The key to successful control of subterranean termites therefore lies in foundation structures which eliminate from the building site all scrap wood, which will serve as food for termites and permit an increase in termite populations. It involves construction of impenetrable foundations, and good drainage and ventilation to discourage termite activity, and requires that structural wood be well above the soil or, if it must be in contact, that it be pressure-treated with an approved preservative. However, it must be remembered that while these recommendations are basic, they will not perform with equal effect under any and all conditions and in all localities. For example, on the upper Atlantic coast a structure on a chain wall or pier foundation properly ventilated and drained is in most cases amply protected. On the other hand, in the semi-tropics or tropics, where termites are favored by high humidities and their populations are high, these precautions have little value.

In recent years there has been an increasing trend toward construction of all-masonry or concrete structures with very little wood used. This would appear to be an excellent method of termite control, but at present the point is debatable. Unless the foundation is of monolithic construction and not subject to cracking, and unless all holes, pipe chases, etc., are properly sealed, hidden infestations can result which are more serious than those occurring in conventional structures. Studding, framing, and other wood can be destroyed, and such damage can be remedied only by tearing out units to determine points of termite entry and drilling the concrete floor to poison the soil. Even where no such wood is used, termites can still damage furniture, rugs, clothing, and other wood and cellulose products. It might be well to point out here that they may bore through products other than those containing cellulose. Lead, aluminum, certain plastics, natural and neoprene rubber, and asphalt are only a few of the materials subterranean termites have been known to penetrate in their search for food.

Where application of preventive structural methods fails to control these insects or where it is impractical, poisoning the soil at points where termites are entering a building may be a highly effective control measure. This procedure is widely used, but there is considerable misuse and misunderstanding about effective poisons and methods of application. The poisons used in past years are almost innumerable, and many fallacies exist regarding some of them.

It has frequently been claimed, for example, that salt will control termites, and, on this premise, that waterfront buildings will not be readily infested. The fallacy of this notion was evident during a termite inspection in 1940 at Ft. Hancock on Sandy Hook, New Jersey, practically every building including those built at the water's edge having infestations of varying severity.

. . 1. ...e` adults of subterranean termite



. . . Damage caused by subterranean termite

There are very few chemicals that have the qualifications of a good soil poison, which are, primarily, permanency and minimum toxicity to plants and animals. The opportunities for improved termite control opened up by the development of new insecticides and equipment now require considerable research to evaluate and adapt them to practical use as soil poisons, wood impregnants, and surface treatments.

Nonsubterranean termites are more important as wood destroyers in certain localities than are the subterranean species. Further, they present a greater problem because of the greater difficulty of control.

These termites are widely distributed over the world, reaching their optimum development in semi-tropical and tropical climates. In this country they are confined to the extreme southern region--in fact, to a narrow strip near the coast, from Virginia around to northern California. They are particularly severe in southern Florida and on the Florida Keys, and, to a slightly lesser extent, in southern California.

As their name implies, nonsubterranean termites, which include drywood, damp-wood, and rotten-wood species, have no contact with soil but rather attack wood directly. It is for this reason that they are, in a sense, more difficult to combat than the subterranean forms. There is little evidence of attack until damage occurs. There are no conspicuous colonizing flights, such as in the subterranean group, to indicate the presence of an infestation. However, such flights are made, and during the flights males and females shed their wings, pair off, and bore into the wood, sealing the entrance with a plug. Tunneling of the wood is begun immediately and increases in intensity as the colony grows. There are only two castes represented--the reproductives and the soldiers. While colonies are small compared to the subterranean species, considerable destruction is caused by the species before evidence of activity appears. One of the best signs of damage is the tiny pellets of partly digested food that the termites expel from their galleries. This may be of little value as an indicator, however, if the infestation is in inaccessible places.

This group of insects, particularly the dry-wood termite, is probably best known for its damage to furniture, although any cellulose material may be attacked, including woodwork of buildings, transmission line poles, lumber, paper, cloth, insulation board, etc. The problem is most severe in the Tropics--in Key West, Cuba, Puerto Rico, Panama, and Hawaii. Dry-wood termites are the No. 1 problem in wood deterioration in these areas.

Various methods of control have been tried for many years, ranging from the injection of insecticides into furniture with a hypodermic needle to the enclosing and fumigating of an entire building and its contents within a tent. Use of fine screen has been recommended to prevent entry of termites into buildings, and the application of heavy coats of paint has been employed to deter outside attack. Inorganic stomach poisons or contact insecticides, principally dusts, have been largely used for controlling infestations. These measures have been effective only to a limited extent, have been of

a temporary nature, and often have been impractical in application. As in the case of subterranean termites, recent development of new insecticides and wood preservatives gives considerable promise of more effective and permanent control. There is much yet to be learned about the methods to use in obtaining penetration of residual insecticides into the wood in order to control active infestations and to prevent future attack. In localities where the problem is particularly severe, preventive treatments of a permanent nature may be applied to all wood used in new construction or for replacement purposes.

Wood Borers

Several species of wood-boring beetles, including largely the groups known as wood borers and the powder-post beetles, present special problems in the deterioration of wood in waterfront structures. Some may attack wood in the green log stage, or the green lumber upon which bark flitches remain. They may survive air-drying treatment and, if the wood is utilized within one or two years, will continue their activities within structures. Most of the species complete their development from worms or larvae to adults within 2 years, emerge, and never reattack. A few will reinfest the wood and continue their destructive activities indefinitely. While the extent of damage caused by this group of insects is not well known, it nevertheless creates undesirable problems. Emerging borers make holes from 1/8 to 1/4 inch in diameter in the surface of the wood containing them, and if paneling, wall board, flooring, or other material is laid over this wood, they will bore through it also in order to emerge.

By far the most destructive beetles are those classed broadly as powder-post beetles which attack seasoned wood. These attack the wood directly either during storage on the lumber yard or in a structure and continue their activities, breeding one generation of progeny after another until the wood is completely destroyed. Some damage wood rapidly, others slowly but surely. While most of the species are of world wide distribution, only a few have been studied sufficiently to determine their habits and control.

The group known as Lyctus powder-post beetles has caused concern in the wood-using industry for many years. This tiny black or brown hard-shelled insect attacks principally the large-pored hardwoods such as oak, hickory, ash, walnut, etc. While the green wood may be attacked in the lumber yard, it is usually the finished product that is infested, and destruction is greatest when products are in storage. It is impossible to estimate accurately the total amount of destruction caused by these beetles to flooring, wood gunstock blanks, cots, furniture, tool handles, dunnage, and other items in this country alone. It is equally severe in other parts of the world and several countries have recognized the problem to the extent that legislation has been employed in an effort to prevent serious losses and keep the insects under control.

Another powder-post beetle known widely for its destructive activities and one which is becoming increasingly important is the old house borer or

Hylotrupes. The insect is rather large in both the larval and adult stages and makes channels and holes in the wood up to 1/4 inch in diameter. It attacks all soft woods and is found principally in large timbers such as joists and beams. Due perhaps to the increased use of sapwood, pointed out earlier, it appears that this insect is becoming increasingly common in the United States. This very point is brought out in a recent report from Sweden which presents the findings of a survey of wood-destroying insects and also states that the cost of repairing existing damage caused by this borer in Sweden would amount to over $25,000,000. Reports from other parts of Europe, North and South Africa indicate a similar situation in these areas.

The borer has not been so intensively studied in this country. However, it has been found in outdoor structures, such as in bridge timbers, poles, and piers, as well as in all parts of dwellings, warehouses, and like structures. The size of the insect added to its life cycle of from 3 to 7 years, means the rapid destruction of wood. High temperatures and humidity favor its optimum development.

There are several other species of powder-post beetles which because of small size and inconspicuous activity attract little attention. Nevertheless, as a whole, they likewise cause severe damage. It is unusual to find foundation timbers, particularly in basementless structures, free from attack by one or more of these species. Unfortunately, presence of the insect is not detected until failure of timber is noted and, as frequently happens, the causal agent is ignored, the timber is replaced, and the general infestation continues.

One insect, known as the wharf borer, stands apart from the powder-post beetle in its relationship and habits. It is usually associated with decay fungi in very moist wood and under such conditions has been observed hastening the destruction of piling, decks under wharves, boardwalks, telephone poles, fences, piers, and even buildings. It has been reported from numerous points in the United States, particularly along the coast, and from other parts of the world, and, although it has not received a great deal of study it is known to be capable of doing considerable damage.

Very little is known regarding the biology and control of this insect. Treatment of wood with preservative deters its activity for a period of time, but it will attack wherever impregnations are poor or leaching of chemicals has begun.

There is much yet to be learned of the biology and practical prevention and control of wood-boring beetles. It is believed that the residual action of new synthetic insecticides offers considerable promise in this regard. However, the method of introducing these chemicals into wood to reach deep infestations remains a problem. Fumigation of small buildings, furniture, or tool stock with methyl bromide is very effective but is limited because no protection from future attack is offered and this method cannot be used for large buildings or their contents. In some cases the impregnation of wood with a preservative by soaking or pressure treatment offers a worth-

Fig. 4. Damage caused by old house borer

while preventive approach. Chemical formulations and methods of application for control of these insects should be investigated.

NEED FOR RESEARCH ON PROBLEMS OF DETERIORATION

In the above discussions on various problems of deterioration, it has been repeatedly pointed out that there is a great need for additional research.

In the recent past, wood has been a very plentiful commodity of high quality. Interest in the protection of wood products has therefore not been great. Consequently, until recent years research on wood-destroying organisms has been somewhat limited and in many cases appears to have failed to keep abreast of the need for the preservation and conservation of wood products for the building industries. With the decrease in the timber supply, the development of demand for innumerable wood products, and the high cost of such products due to increased cost of the raw material and its manufacture, there has come a realization of the need for research designed to protect this valuable resource.

Advancements in the fields of chemistry and engineering have provided promising materials for study. During World War II and since, there have been revolutionary developments in the chemical industry and in the production of potent residual insecticides, such as DDT, BHC, chlordane, toxaphene, heptachlor, and others, which far exceed most of the older insecticides in effectiveness. Considerable progress has also been made in the development of new equipment, including numerous types of thermal fog generators, mist blowers, and improved hydraulic sprayers, to be used in the surface application of these insecticides. There have been also marked improvements in methods and equipment for impregnating wood with preservatives.

Outstanding though they are, these developments merely provide a tool for the control of the various organisms destructive to wood. Each insecticide must be investigated thoroughly to determine the formulation most effective and most practical in a particular situation. Each formulation must be compared with standard treatments and evaluated on the basis of performance and cost.

A most important consideration, however, is the need for basic biological studies of the destructive organisms involved. In the haste to obtain results--a characteristic of much of our research in the past decade-- there has been a tendency to overlook the fact that development of effective control measures is dependent upon a knowledge of the behavior of the organism for which the control is directed. Thus, it appears that much of the research of past years has followed a hit or miss pattern.

Fundamental research on the biology of the organisms, including life history, habits, and the relationship to the environment, is essential in order that control measures may be effective and economical. Among the insects, a few species of our native termites and the powder-post beetles have been most extensively studied. Little is known, however, about many species of

termites, powder-post beetles, and the numerous wood borers found in this country. The field of wood deterioration in the tropics is virtually unexplored.

There has probably never been a period in our history when interest and progress in the utilization of wood has been greater than at present. Conservation and protection are integral parts of this advancement, and research in these fields at this time can contribute much toward the progress being made.

(Contribution from the Bureau of Yards and Docks)

DESIGN FACTORS AFFECTING DETERIORATION OF MARINE STRUCTURES

by Ralph C. Stokes

The engineer is acutely aware of the destructive forces which are ever at work on marine structures. Many centuries of experience have demonstrated the severity of the attack which involves chemical, physical and biological processes. The battle to overcome the damaging effects has taken many different turns and made use of every known available construction material. None of these is exempt from the ravages of all types of deterioration, but each is vulnerable to one or more of the destructive processes.

Much can be done to extend the useful life of waterfront structures by proper attention to arrangement of parts, selection of materials, choice of optimum shapes, and the use of protective applications. The three principal construction materials, timber, steel and concrete can all be used effectively if the results of experience are kept in mind. The purpose of this paper is to present some of the methods which have been adopted by the Bureau of Yards and Docks to obtain maximum length of life at a minimum overall cost.

Timber Construction:

No doubt the first crude structures built to accommodate shipping were of wood. The rapid deterioration which followed probably led to the observation that certain species were more resistant to decay than others. Perhaps the next discovery was made by the Phoenicians, who practiced the charring of wood to obtain greater life expectancy.

It is interesting to note that wood preservation, in a modern sense, did not begin in earnest until the second quarter of the nineteenth century. Although the present method of injecting creosote into wood under considerable pressure was devised by John Bethell in 1838, the method did not attain commercial importance until 1875.

Hazards to Timber Construction:

Timber waterfront structures suffer principal damage from the hazards of decay, marine borers, abrasion and fire.

By far the greater portion of the damage done to timber results from the action of decay and marine borers. If timber is continuously submerged, there is no decay. However, marine borers must be considered a menace at most locations on salt water. Thus for marine structures, the borers threaten timber below water, decay is active above water, and both do damage in the tide zone.

Methods of Protecting Timber:

The three general methods used for the protection of timber are coatings, armors and injected preservatives. No really effective coating has been developed to date. Armors give efficient protection so long as they remain unbroken and extend from a level above high water to one below harbor bottom sufficiently far to guard against the possibility of scour.

The process of protection by injected preservatives is the most generally used because it has the advantage of affording protection against decay, insects and marine borers. The preservatives include soluble and insoluble salts, creosote oil, and creosote coal tar solutions. Soluble salts are not reliable if the timber is exposed to leaching. The best results are obtained from pressure treatments which produce complete penetration by the preservative. Physical damage to piles during handling and driving must be avoided in order to realize maximum benefit of the preservative treatment. Boring and cutting of piles below high water encourages entry of marine borers. Deterioration is less rapid for pile bents capped with single timbers than for those framed by cutting the pile heads to receive a pair of cap clamps.

Abrasion damage applies principally to exposed decking and to the outer faces of fender piles. There is often ample evidence to support the belief that no extended usefulness is obtained by treatment of deck timber to prevent decay, on account of the physical destruction caused by wear. Covering of the exposed surfaces with more resistant materials is the only practical solution for abrasion. The life of wood fender piles can often be materially increased by the provision of metal rubbing strips on the contact areas.

The fire hazard must not be overlooked in design. The principal protection consists in segregating a structure into several units by firewalls or bulkheads extending from the underside of the deck to a level below the low water line. The provision of openings in the deck for foam nozzles are often provided for additional protection.

Concrete Construction:

Concrete is generally considered to be the most durable material available for the building of waterfront structures. This idea probably stems from the fact that cement was made in the time of the Romans that remained stable in sea water for hundreds of years. Modern Portland cement apparently lacks such chemical stability in sea water and its use in concrete require careful control.

The Bureau of Yards and Docks has under test at Portsmouth, New Hampshire, prototype concrete pile specimens 14 inches square by 13 feet long. A total of 96 specimens were hung in the tide zone during the years 1925 through 1933. Each of these specimens varied in some particular, either in the kind of cement, proportions of the mix, type of aggregate, use of an admixture, surface treatment or special type of reinforcing. Various

types of Portland cement, Alumina Cement and superfine Portland cement were used in varying proportions from 3 bags per cubic yard to 9½ bags per cubic yard.

From the long time tests at Portsmouth plus observations made on concrete Naval structures located in many parts of the world the following conclusions have been drawn: The concrete appears to fail through disintegration of the cement which progressively loses its bond and cementing power. This disintegration occurs more rapidly in some Portland cements than in others of the same type. Alumina cement has not demonstrated a superiority over Portland cement. The admixtures which were used did not appreciably retard deterioration of the concrete nor did the use of silica sand improve the density of the concrete by chemical action with the cement. Improved density can be achieved by the use of well graded aggregates.

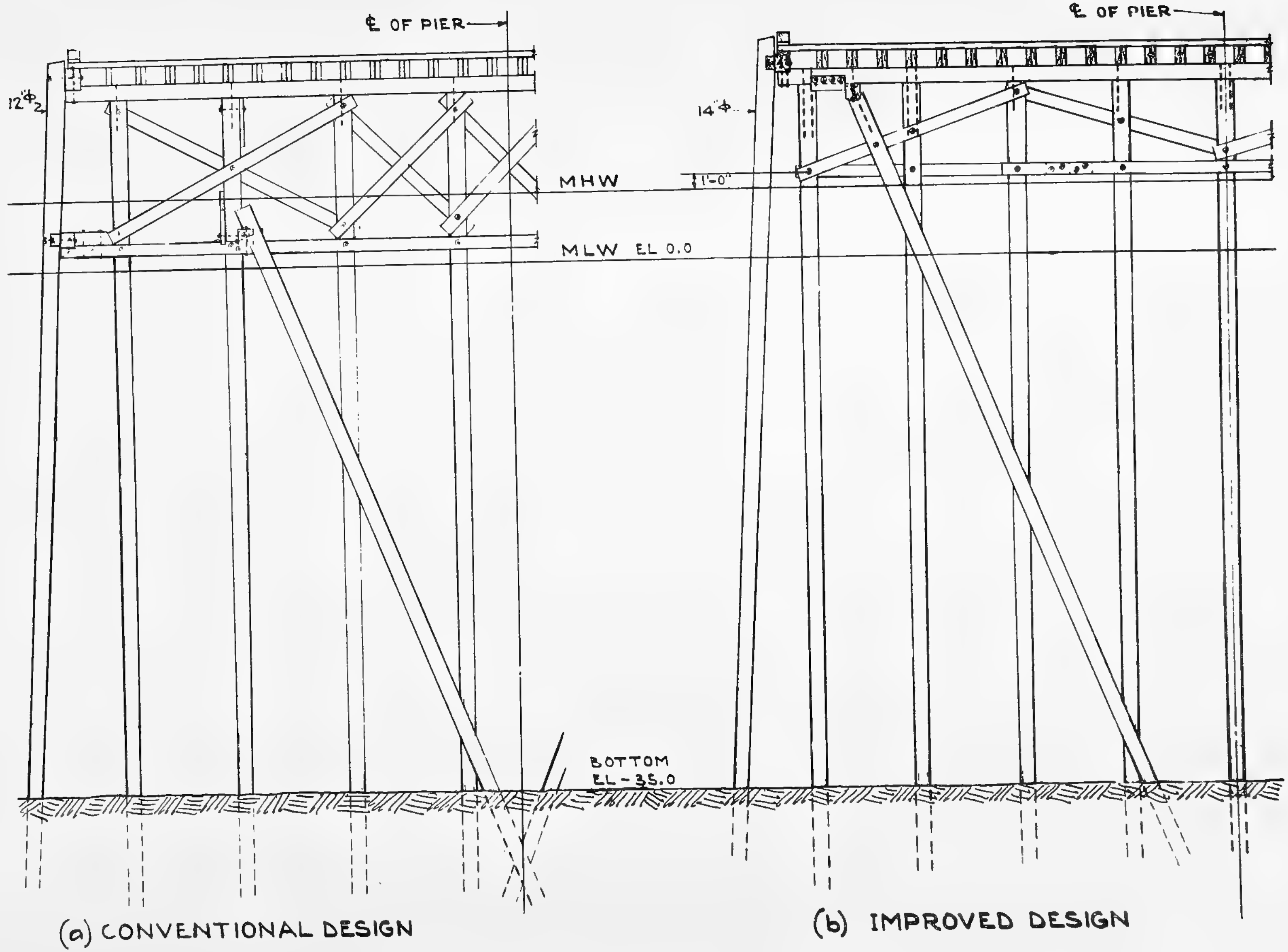
Surface density is an important factor in the life of concrete piling. It can be improved by the use of very smooth surface formwork, plus form vibration. No appreciable advantage is gained by the use of corrosion resistant reinforcing. Increased clear cover over reinforcing is a more economical solution.

Comparatively rich mixes of concrete are required to prevent the deterioration of concrete in the tide zone. It is interesting to note that the most perfect concrete pile specimen hung at Portsmouth contains a mixture of cements from four different producers. The concrete contains 6½ bags of cement per cubic yard. Two other specimens in excellent condition after 27 years contain 9 bags of cement per cubic yard of concrete. The water-cement ratio has a marked influence on the durability of concrete. This is evidenced by the fact that the less the slump the more resistant the pile specimens have been to deterioration. The selection of both fine and coarse aggregates that are known to be chemically stable with cement, in the presence of salt water, is essential.

Steel Construction:

Although the process of smelting iron has been known for thousands of years, it was 1840 before the principal support of a waterfront structure was formed of cast iron. Solid wrought iron piles were installed about 10 years later, while steel shapes were not used until about 1870.

Although service records indicate that cast iron, in the form of cylinders or piles, is the most durable material currently available for use in waterfront structures, it has received little consideration during the last 35 years because of its lack of tensile strength and comparatively high first cost. Reports on solid wrought iron piles indicate a service life comparable to those of hollow cast iron. However, the wrought iron or steel bracing members required in connection with either wrought or cast iron piles and cylinders have required rather frequent replacement. This replacement cost, rather than the high first cost of cast or wrought



TIMBER PIER CONSTRUCTION

FIG. 1

iron supporting members, accounts for the disuse of an otherwise satisfactory material.

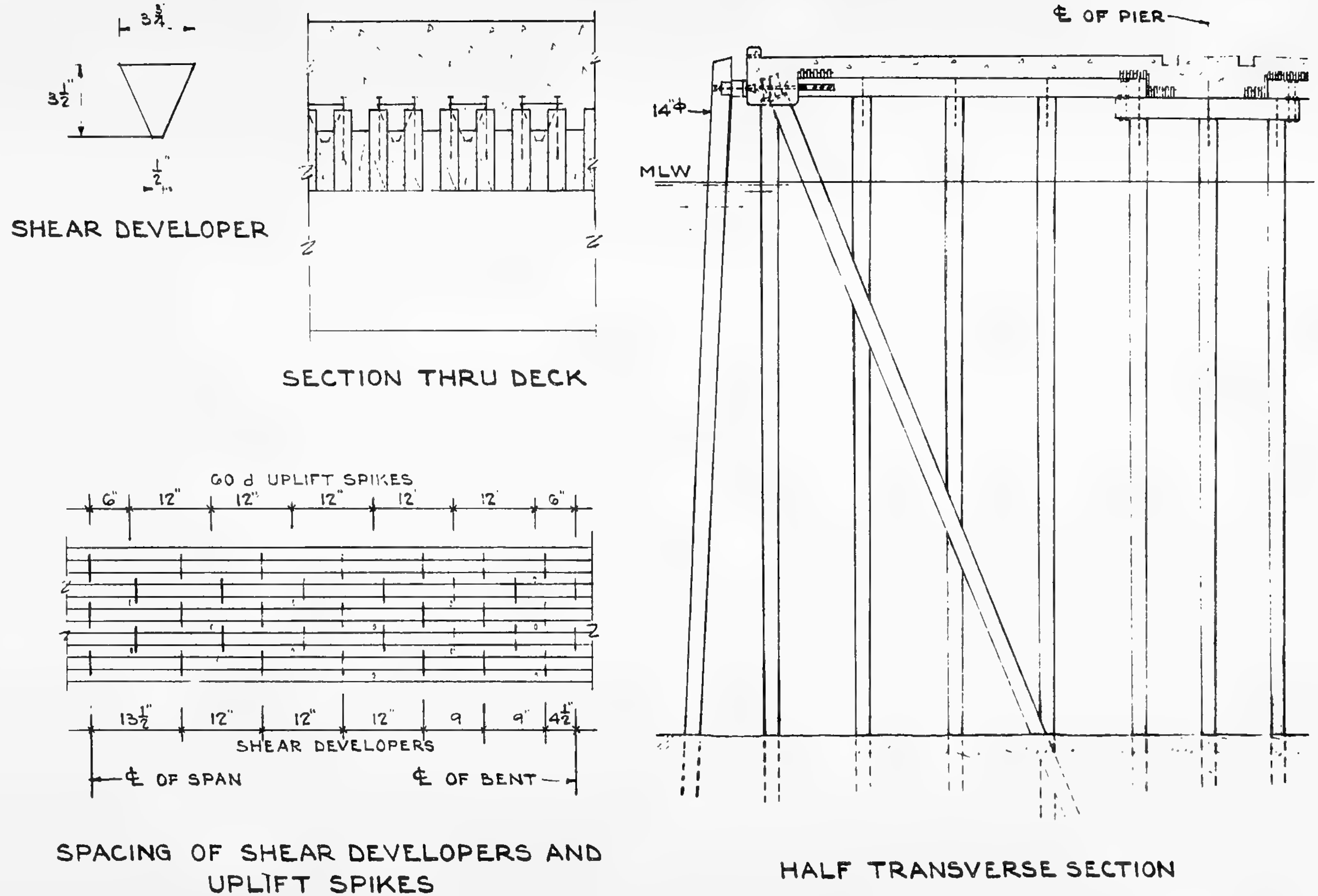
Following the rapid expansion of the steel industry from 1890 through 1912, many steel pipe piles and cylinders were used to support waterfront structures. In the latter half of this era, steel deck framing was also used quite extensively. The comparatively rapid deterioration of these structures by corrosion and the resulting maintenance or replacement costs soon curtained this type of construction. With the introduction of steel sheet piling and the expanding use of steel "H" piles, much experimental work was done in an effort to develop a more corrosion-resistant steel. Copper bearing steel was introduced both in Europe and the United States as being at least a partial answer to the problem. Records, however, indicate that in many locations little increase in resistance was apparent. Modern steel sections can be used to advantage in many locations where timber or concrete sections cannot be used. The useful life of a steel structure can be materially extended by the adoption of a simplified design and the initial protection afforded by coatings or envelopes located in the zones of critical corrosion. Cathodic protection, which is now under test, promises to retard corrosion in the tide zone on both old and new steelwork. However, it is not effective in or above the splash zone.

In order to illustrate better the design techniques which will aid in solving deterioration problems a series of illustrations are given of both pier and bulkhead construction.

In general, all open type marine structures, with free tidal movement beneath, are subject to more severe exposure than those of the closed type which are exposed only along the exterior faces of the structure. Figure 1 illustrates two timber pier designs. Figure 1a is the conventional design wherein the lower level of bracing is located just above mean low water and is subject to maximum exposure in the tide range. Figure 1b shows an improved design. Here the bracing system is raised above high water level and the connections for the batter piles are made at the level of the main transverse timber caps. The life of the structure will thus be increased by removal of the bracing and fittings from the zone of critical exposure.

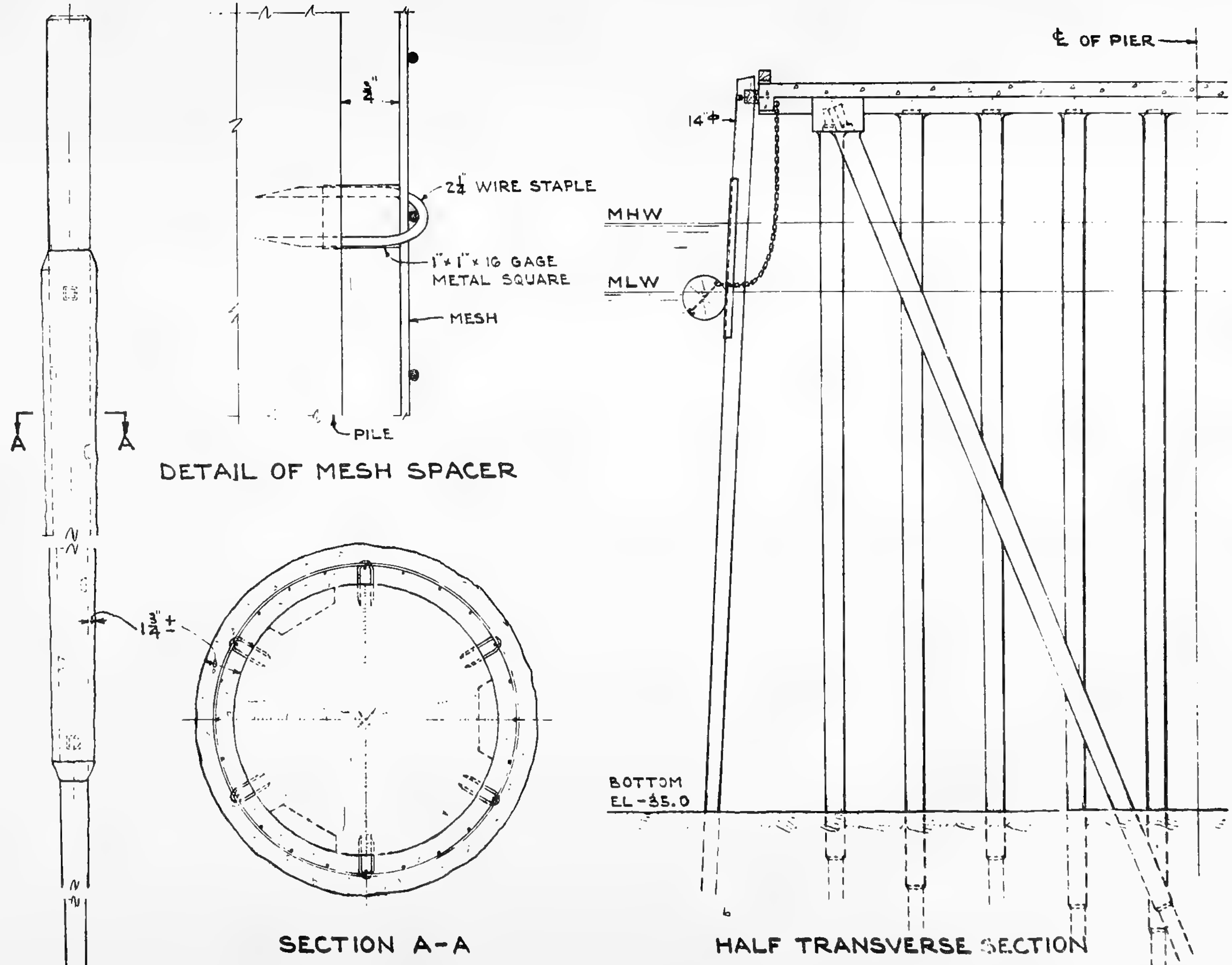
A timber pier with composite deck is shown in Figure 2. In this example, there is no lateral bracing. Stability is provided by a system of A-frames. These are formed by embedding the outer vertical pile and the batter pile, in each transverse bent, in a concrete beam. The composite deck protects the timber caps from exposure to weather and the only members exposed in the tide zone are the round piles.

Some piers require the use of very long piles. In this case, timber piles with concrete jackets can be used to advantage as illustrated in Figure 3. The concrete jackets perform a dual function: First in providing a large increase in pile stiffness, thus eliminating the need for bracing, and second as armor, providing protection from marine borers. The jackets are applied on untreated piles prior to driving by depositing an encasement

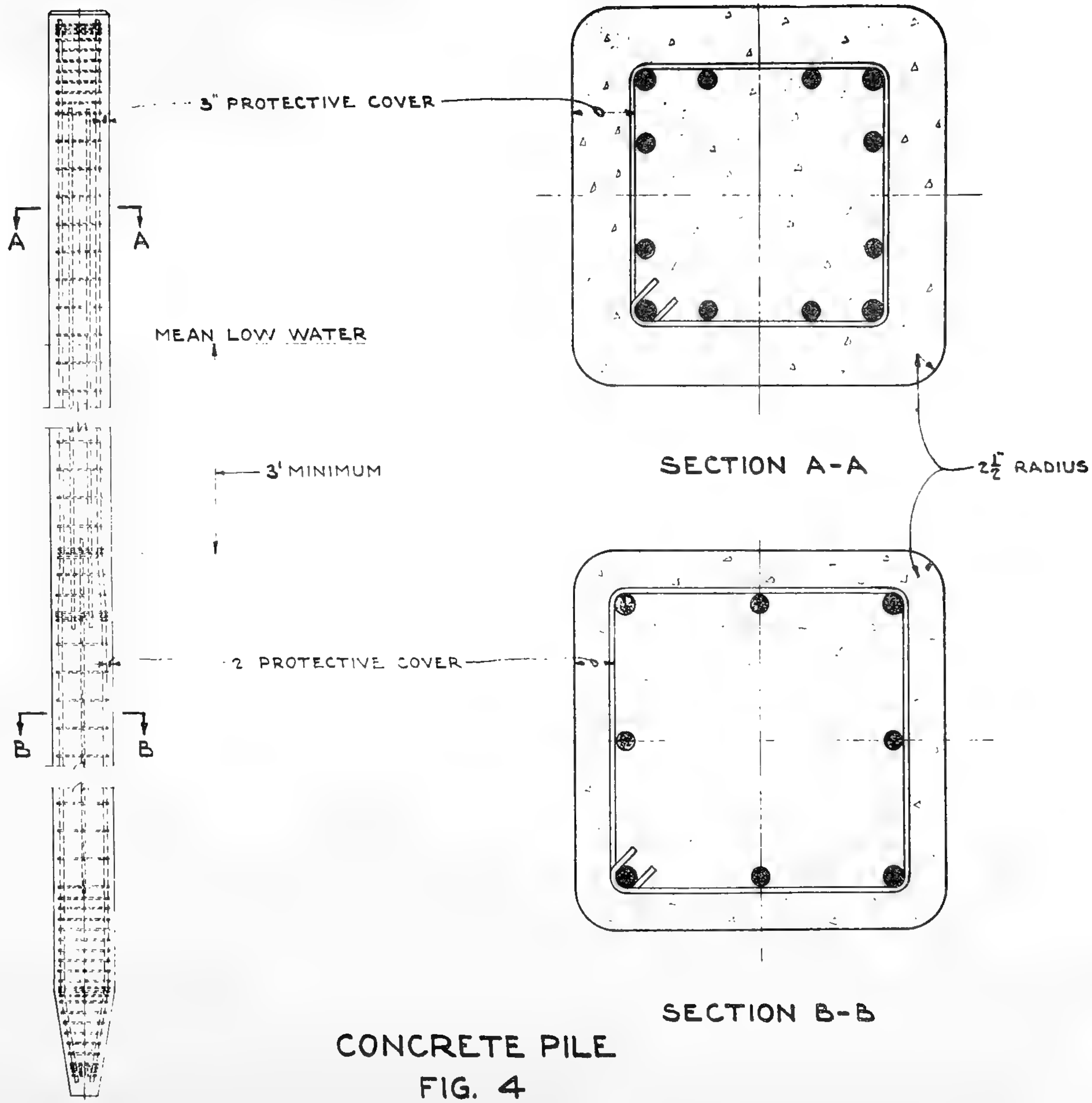


TIMBER PIER- COMPOSITE DECK

FIG. 2



TIMBER PILES - CONCRETE JACKET
FIG. 3



CONCRETE PILE
FIG. 4

of cement mortar about 2" thick over the surface of the pile by means of pneumatic equipment. This type of protection for timber piles has been used with success on several large navy piers.

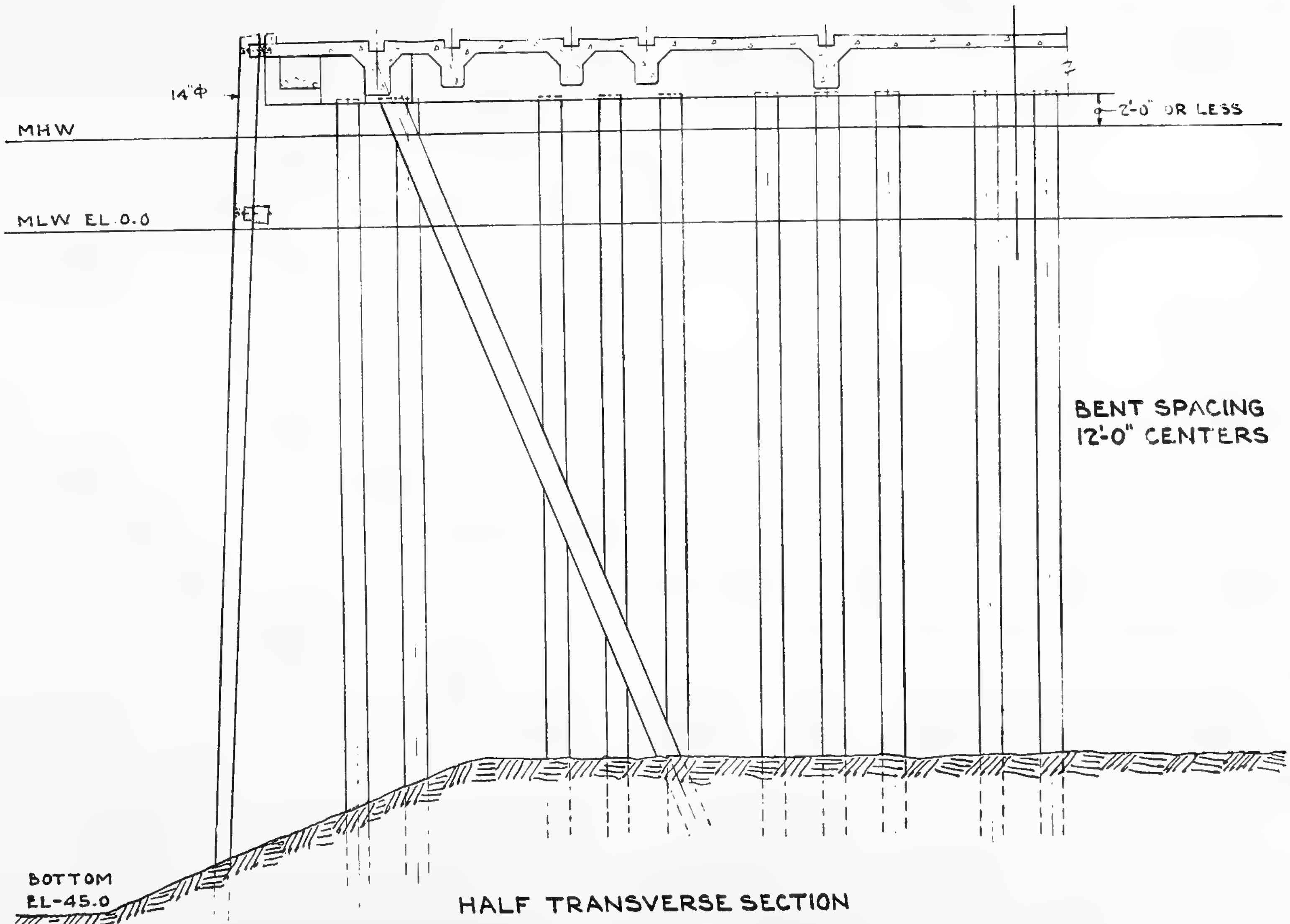
Figure 4 shows a concrete pile designed for longer life in the tide zone. In the illustration, it will be noted that a two inch minimum thickness of concrete cover is provided over the steel for the lower portion of the pile. Above this level, the longitudinal steel reinforcement in the pile is bent so that the concrete cover is increased to a minimum thickness of 3 inches. Since square corners are more vulnerable to deterioration by both chemical and physical processes, the corners are rounded to a minimum radius of $2\frac{1}{2}$ inches.

Figure 5 illustrates a conventional concrete pier. Unless the deck is located well above high water, the lower surfaces of beams and girders will be subject to the deteriorating effects of saltwater spray. The many corners involved in this design tend to promote attack on the reinforcing steel.

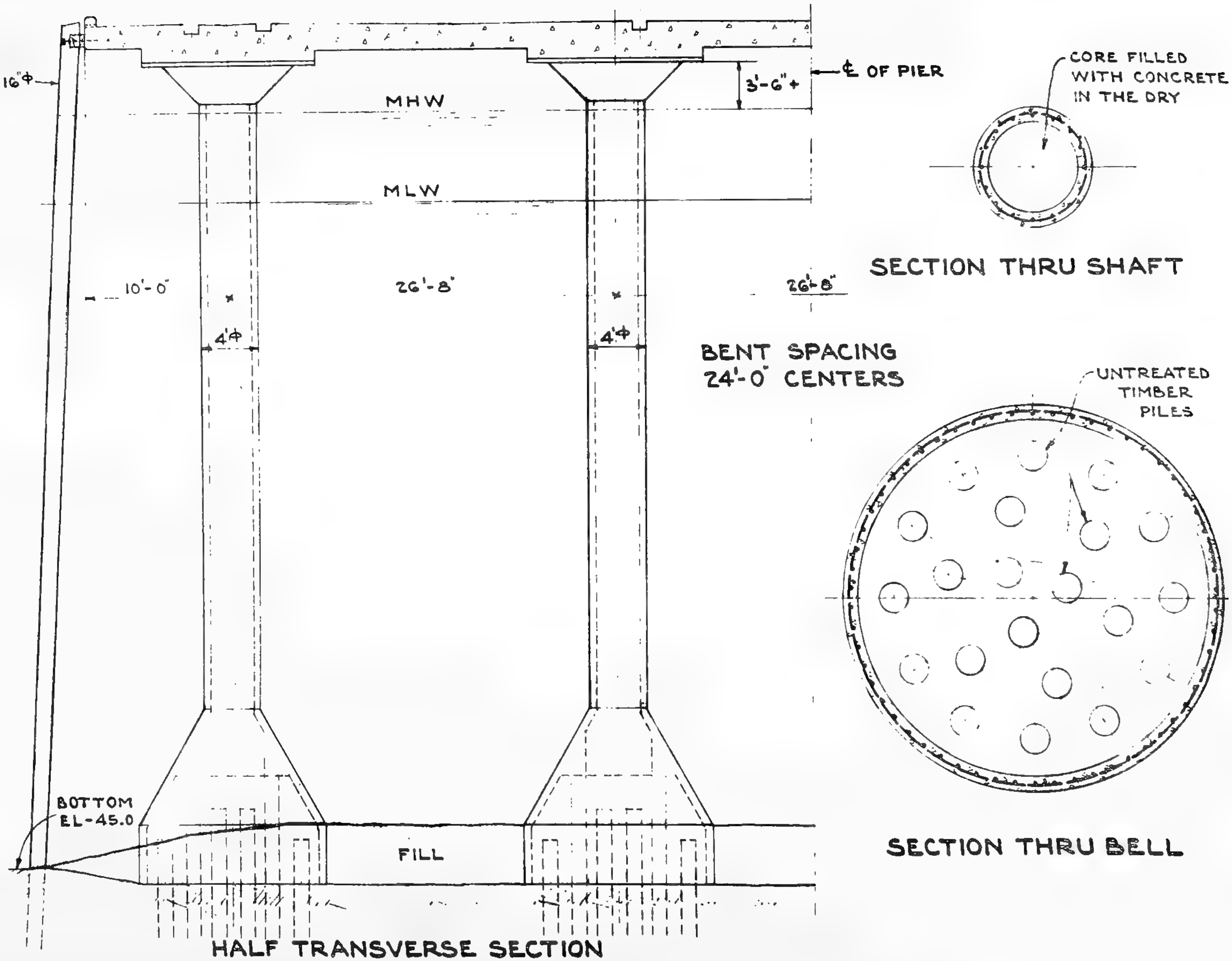
Figure 6 shows an ideal concrete pier design. The circular cylinders have optimum shape for resisting attack by saltwater and for minimum force from wave action. If the cylindrical shells are cast with the aid of smooth metal forms and adequate cover is maintained over the reinforcement, a long life should result. The number and area of vertical supports is held to a minimum. The flat slab construction has no deep transverse girders nor longitudinal beams exposed to salt water spray. Untreated timber piles may be safely used as supports beneath the cylinder bells.

The conventional design of a steel pier is shown in Figure 7a. Lateral stability is provided by batter piles in combination with a system of cross bracing. Rapid deterioration of this bracing will occur even though the usual protective coatings are applied. By way of contrast, Figure 7b shows a steel pier without batter piles or bracing. Lateral stability is obtained by rigid-frame action. The timber-concrete composite deck gives wide distribution of local lateral loads to several bents so that lateral deflections are reduced. The vertical piles have concrete jacket protection in the tide zone for maximum longevity, where additional stability is required, A-frames can be added beneath the center of the pier.

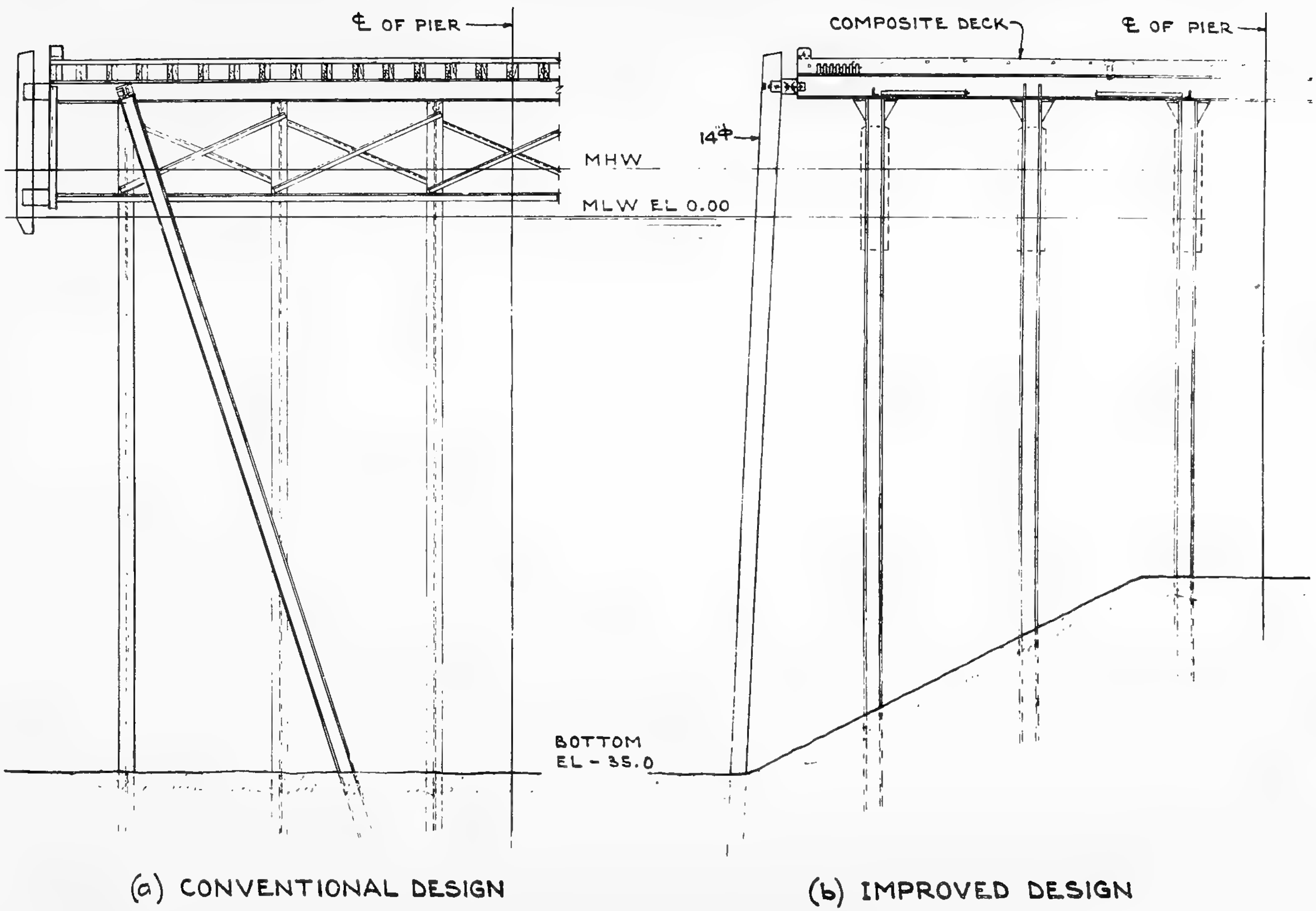
A practical method for installing jackets on either timber or steel piles is shown in Figure 8. It is equally applicable to existing piles or to new construction. The two halves of the form are separated by rubber gaskets which are compressed as the form is locked together, thus providing for self-stripping when the pressure is released. With the form secured in position around the pile at the desired elevation, coarse aggregate is deposited to fill the form after which a special grout with admixture is introduced at the bottom of the form. As the grout rises to the top, the water in the form escapes through a series of vent holes and a complete filling of the voids with good grout is achieved.



CONVENTIONAL CONCRETE PIER
FIG. 5



IDEAL CONCRETE PIER
FIG.6

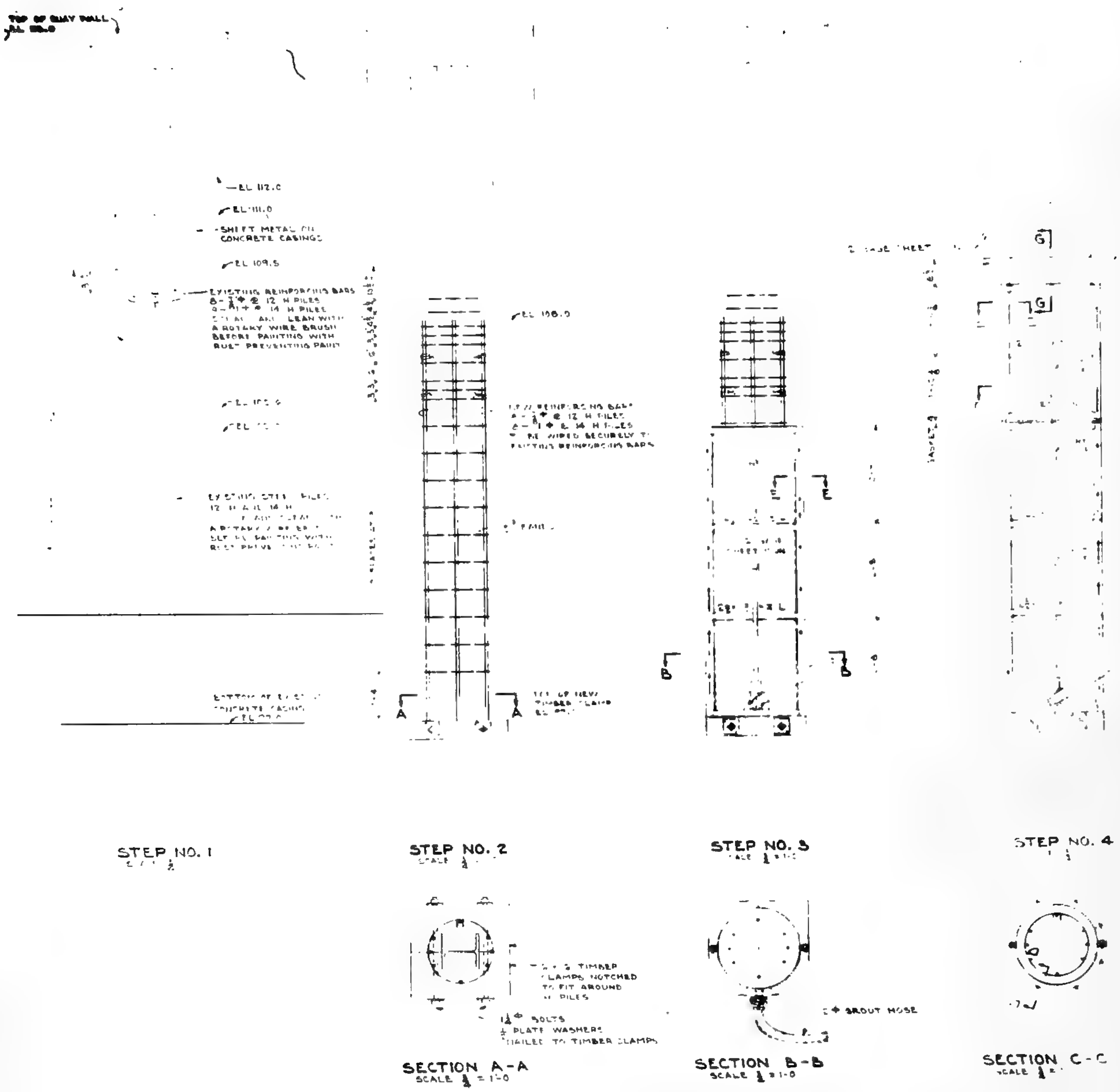


(a) CONVENTIONAL DESIGN

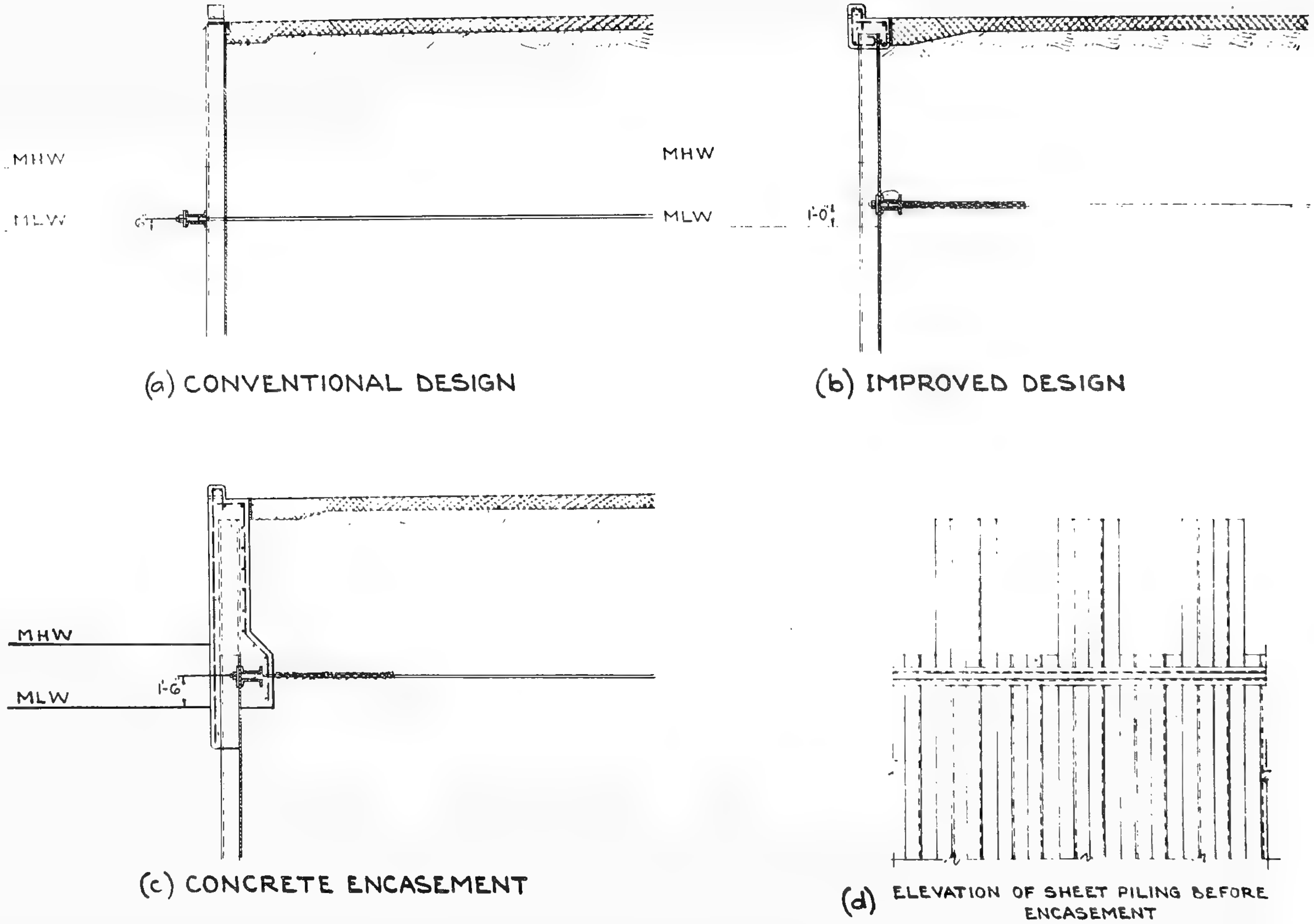
(b) IMPROVED DESIGN

STEEL PIER CONSTRUCTION

FIG. 7



REMOVABLE FORM FOR CONCRETE PILE JACKET
FIG. 8



BULKHEAD CONSTRUCTION
FIG. 9

The last two illustrations relate to bulkhead construction. Figure 9a shows a section through a conventional bulkhead. The steel wale is located for erection convenience on the outside of the sheet piles above mean low water. A steel cap channel is used in forming the top curb. The steel wale is severely exposed and deteriorates rapidly. The channel cap shares a fate only slightly less severe. The tie-rod corrodes badly adjacent to the bulkhead. By the simple procedure of transferring the wale to the inside face of the sheet piles and protecting the upper channel with con-concrete as shown in Figure 9b, the life expectancy of the wale is greatly increased. Critical corrosion of the tie-rods can be prevented by painting and wrapping the 6 ft. length of rod adjacent to the sheet piles, or encasing it in concrete. A concrete cap and curb built along the top of the sheet piles is far superior to the conventional channel curb. Besides, it acts as a much better distributing beam for the bulkhead system. At locations where corrosion is known to be severe, encasement of the upper portion of the piling in a concrete envelope, as shown in Figure 9c, is necessary. A saving in weight of steel can be made by varying the length of alternate pairs of sheet piles, as shown in Figure 9d.

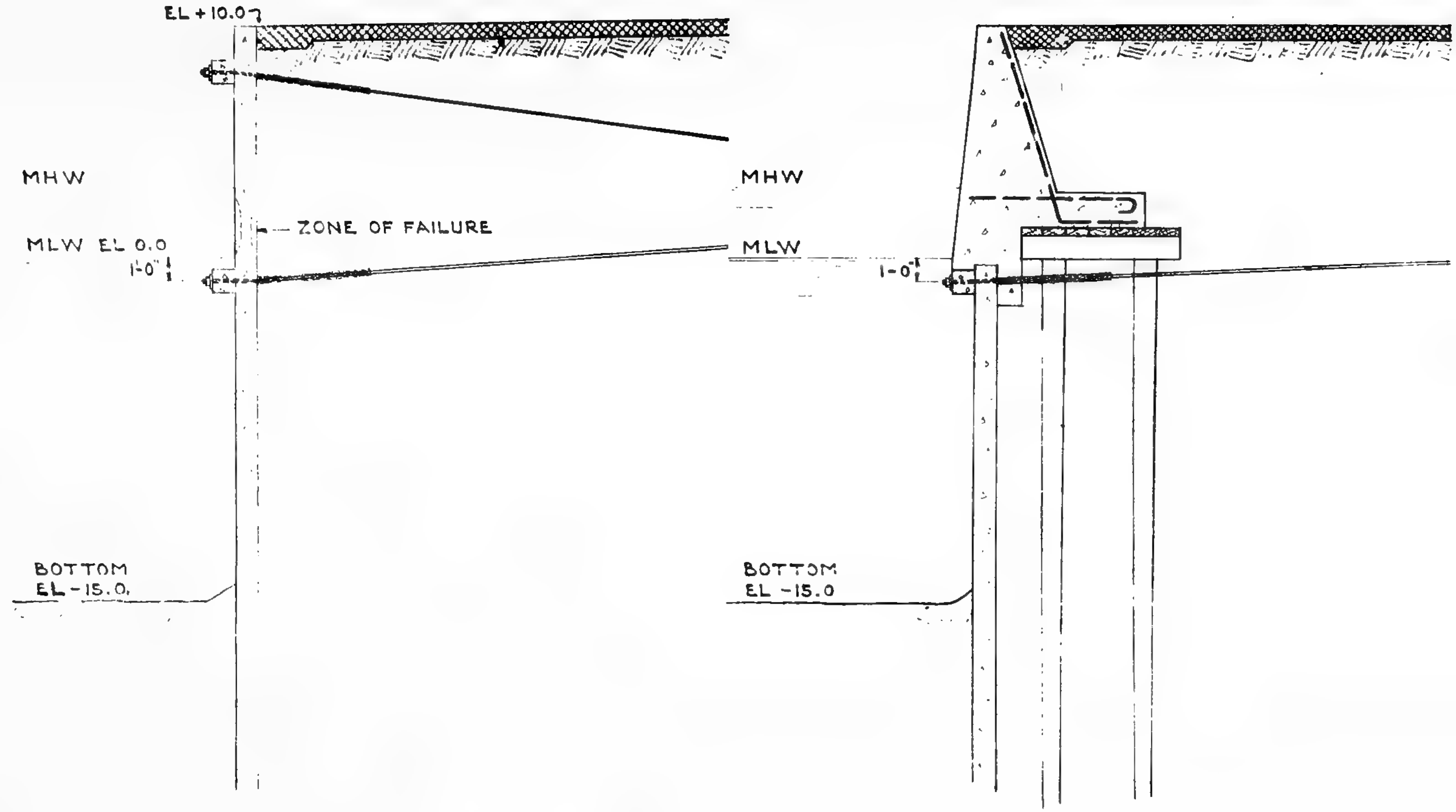
Figure 10 illustrates a bulkhead design which is adaptable to repair at a later date, after having served an initial normal life. In this case, the sheet piles are anchored at two levels because of the high backfill elevation. The lower wale is located on the outer face of the piling, but is about one foot below mean low water to reduce tide zone exposure. At the "zone of failure" shown, the deteriorated areas of the sheet piles permit leaching and escape of backfill material which causes a lowering of the top grade. This type of failure does not endanger the stability of the bulkhead as a whole, because the lower wale and tie-rod system remain intact and retain the original alignment of the lower portion of the sheet piles. The upper portion of the bulkhead can be repaired as shown in Figure 10b. A narrow relieving platform is built behind the sheet piles to reduce the lateral pressures and a concrete gravity retaining well is constructed above the platform. A bulkhead, reconstructed in this manner, will generally last longer than the original construction.

Recommended Design Practices:

The more important lessons learned from experience on the deterioration of timber, concrete and steel waterfront structures may be summarized as follows:

a. Since maximum deterioration occurs in the tide zone the number of structural members located therein should be kept to a practical minimum. The elimination of bracing within the tide range is the first step toward a better design.

b. Round members because of their smaller area and better flow characteristics for wave action generally have a longer life than other shapes.



(a) INITIAL INSTALLATION

(b) METHOD OF REPAIR

BULKHEAD REPAIRS
FIG. 10

c. It is imperative that all steel or concrete deck framing be located above normal spray level.

d. Untreated timber piles should never be used in waterfront structures unless located below the permanent wet line and protected from marine borer attack.

e. The most effective injected preservative appears to be creosote oil having a high phenolic content. For piles subject to marine borer attack a maximum penetration of creosote-coaltar solution is recommended.

f. Salt-treated timber gives satisfactory service when protected from the weather.

g. Boring and cutting of piles after treatment should be avoided. All surfaces so cut require special treatment.

h. Single timber caps have a longer life than pairs of cap timbers dapped into the piles.

i. Untreated timber piles when encased in a gunite armor and properly sealed at the top will give economical service.

j. Concrete to last in the tide zone must have a high cement content; a minimum of 6-1/2 bags per cubic yard is recommended.

k. The lower the water-cement ratio, the more durable concrete will be in salt water.

l. Care must be exercised in the selection of coarse and fine aggregates both for density of grading and to avoid unfavorable chemical reaction with the cement.

m. Maintenance of specified clear cover over all reinforcing steel is of the greatest importance.

n. Smooth formwork and rounded corners improve the resistance of concrete structures.

o. All steelwork in and above the tide range requires the initial protection of a coating or concrete envelope.

Conclusions:

The battle against deterioration may never be completely won. However, the life of marine structures can be significantly extended by applying the lessons learned from experience to their design.

Further progress awaits the discovery of more effective protective materials and the development of new methods for marine borer control.

The sad fact that little progress has been made in the last 75 years should be a challenge to us all.

(Contribution from the Marine Laboratory, University of Miami)

LIFE HISTORY OF TEREDO*

by L. B. Isham

Abstract

Since so little is known of the early life history of larviparous shipworms, the larval and early boring stages of *Teredo* (*Lyrodus*) *pedicellata* De Quatrefages were studied in some detail.

This shipworm, the most common in the Miami area, was cultured in laboratory tanks and used as a source of larvae of known age.

The anatomy of the larvae was studied and compared, in some respects, with other species of *Teredo*.

The free swimming and crawling stages and the early boring stages were described in respect to anatomy and behavior. The development of the siphons and of the early development of the shells and pallets were described.

The mortality rate of these stages was discussed.

The speed of swimming and crawling was measured and descriptive data concerning locomotion were noted.

*This paper appeared in full in the Bulletin of Marine Science of the Gulf and Caribbean 2(4):574-589, May, 1953. Copies of this may be purchased from the Managing Editor, Marine Laboratory, University of Miami, Coral Gables 46, Florida.

(Contribution from the University of Southern California)

THE RELATIONSHIP OF THE AREAS OF MARINE BORER ATTACK TO POLLUTION PATTERNS IN LOS ANGELES-LONG BEACH HARBORS

by John L. Mohr

Los Angeles and Long Beach Harbors comprise somewhat more than 7,000 acres of water of thirty-five foot average depth enclosed by a rock breakwater from the remainder of San Pedro Bay. Terminal Island, built up from a line of mud waddens and low islands and supporting extensive naval and industrial installations, provides several enclosed anchorages opening on the Outer Harbor and protects the waters of the Inner Harbor. The Inner Harbor appears on the map as a six-mile arch of water with approaches from the Outer Harbor at east (Long Beach) and west (Los Angeles) by thirty-foot channels.

Although flushing and current patterns have not been adequately studied, it has been estimated that with roughly 250,000 acre feet (80 billion gallons) of water in the harbor, the daily tidal cycles move about a fifth or 50,000 acre feet of water in and out the breakwater. Accordingly, it might be predicted that any acute effects of pollution would be found in enclosed areas particularly of the Inner Harbor.

Surveys on the effects of harbor pollution have been of two sorts. Under the aegis of the Los Angeles Regional Water Pollution Board, a coordinating agency of the State of California, some 17 agencies concerned with harbor conditions carried, mainly in 1951, an investigation into the sources and effects of pollution in Los Angeles-Long Beach Harbors. Fifty-five stations in Los Angeles and eighteen in Long Beach Harbor were made. An abridged report of the joint agencies is in press. In this investigation the study of bottom conditions made by analysis of samplings by a small orange-peel bucket was carried out by my colleagues of the Southern California Marine Borer Council for the Department of Fish and Game. Secondly, the Council has carried on studies with standard Douglas fir blocks and microscope slide carriers at fifteen stations chosen to represent a wide range of thermal, pollutional and other factors. From these specific data has been obtained on borer activity and fouling in the major areas of the harbor. Finally, the records of the decennial surveys of piling condition in Los Angeles Harbor (the most recent being that of 1946) have been made available by Mr. C. M. Wakeman, Testing Engineer of the Los Angeles Harbor Department.

Degree of pollution in a harbor may be gauged in a number of ways. The actual quantitative determination of particular pollutants would be most desirable. The chemists of the joint agencies' survey found, however, that with practicable survey methods it was not possible to demonstrate certain deleterious substances known to be entering the harbor in considerable amounts at specific points. The effects of such pollutants may usually be noted by their depression of the dissolved oxygen index, in-

creased biochemical oxygen demand, or even the presence of hydrogen sulfide. However, as with inland pollution, the alteration of the plant-animal associations of various types of waters constitutes the most generally reliable quick indicator both of deterioration and of recovery. With the harbors which our group has investigated, it is the animals studied rather than the more inconspicuous plants which have proved more useful in this respect.

Not all of the harbor animals are likely to be significant in formulating a zoological index of harbor pollution. The floating population or plankton will be perceptibly altered, particularly diminished in a somewhat selective manner, but except where flushing is much reduced, the pollution effects will be rather minimized. Moreover, the mortality of plankton nets, which are both relatively fragile and expensive, is a deterrent to the use of a plankton index in those reaches seriously contaminated. The strong swimmers or nekton, in the harbor mainly fish, also could be ranged into a rough equivalent of the spectrum from trout to carp of inland waters, but a number of practical considerations gravitate against their use for harbor studies.

Two important ecological groups remain which are immediately affected by pollution: a) the forms fixed to or moving sluggishly about the bottom and b) the fauna of pilings, floats and fenders, animals either attached or of limited movements. Of these two biotas, it is the bottom fauna or benthos which is the more profoundly modified by whatever toxicants occur. At the bottom fresh supplies of oxygen are ordinarily farthest removed so that lethal levels are reached most quickly. Here, in addition to the killed animals belonging to this level, settle the victims of unfavorable conditions above and here the sulfur bacteria accumulate in any sludges which may result. Any hydrogen sulfide generated prolongs lethality beyond the primary effects of contamination. Further, there is a strong possibility that pollutants which might otherwise be dissipated by tidal flushing may be incorporated in the sludge preventing re-occupation of the beds by animals from adjacent still productive areas. The findings of the joint agencies' survey are consistent with these generalities. Eight separate areas of the harbors may be considered to be derelict zones. From bottom samples of these areas no living animals were found by use of a low power dissecting microscope. One of these areas lies at the "keystone" of the arch of the Inner Harbor in Cerritos Channel. Here the movements of successive high tides meet so that each half of the arch in effect comes to a dead end. The remaining seven are dead end channels only two of which face on the Outer Harbor. Zone 1 in Watchorn Basin may be affected by neighboring naval establishments and presumably is polluted by domestic discharges from U. S. Coast Guard Moorings and three private establishments which together have an estimated maximum population of 600 persons. The extent of the derelict bottom here is apparently very limited. Zone 2, Fish Harbor, has a concentration of fish-processing plants which at the peak of canning season turn Fish Harbor itself and adjacent waters into a virtually opaque, off-color, foul-smelling suspension.

The remaining derelict zones are within the Inner Harbor where dead end slips receive large amounts of pollution, mainly of industrial origin, but in each case including domestic sewage some part of which is often raw or nearly so. It may be noted that next to some of the derelict zones very high numbers of living animals may congregate as though areas with just tolerable concentrations of pollutants are bordered by belts high in food for these forms or for the microbes on which they depend. In such beds it has been the marine worms or polychetes which have been most abundant. From work on the bottom faunas of Los Angeles-Long Beach, Avalon, New Port and San Diego Harbors, the Council's biologists conclude that the polychete worms provide more clear indications of conditions of marine pollution than do any other group of animals. This is consistent with the findings of Prof. Francis Filice in San Francisco Bay. In general the benthic arthropods and mollusks have proved to be enough more sensitive to be too reduced in numbers to be useful index animals.

Mr. C. M. Wakeman's periodic surveys have shown that at the peak of harbor activity in World War II, pollution was so intense in the Inner Harbor that borer activity was checked in an area which would include and join Zones 3 to 7. Determinations of dissolved oxygen were frequently zero for much of the area and positive sulfide readings were obtained from the water. "In 1940 the Industrial Hygiene Service reported excessive absences from work among fish cannery workers as a result of conjunctivitis caused by hydrogen sulfide." Throughout the war years complaints were made by military authorities about paint damage and corrosion of their harbor equipment. As late as 1948 the U. S. Corps of Engineers estimated the "unnecessary damage" to harbor installations, shipping and industry would reach $2,000,000 annually. But by 1948 the harbor was already less polluted and serious borer damage was observed again within the Inner Harbor, damage which has been increasing since that time.

Conditions in the harbor during the joint agencies' surveys and those of the Borer Council may perhaps be considered to be approaching a fairly stable baseline. Although pollution is high enough to raise corrosive action significantly above that of ordinary seawater, much further improvement will be won only by very persuasive measures, educational or otherwise. On the other hand, agencies now in existence and the balance of interest along the waterfront may be counted upon to hold the line against much additional pollution.

With this background we may examine the results of the standard block survey. Limnoria tripunctata and Teredo diegensis had for the most part a parallel distribution in 1950-1951 and, from spot checks, have one today. In contrast with World War II conditions when most of the Inner Harbor was free of borer activity, only Station C is now without either gribbles or shipworms. Station C receives the runoff of Dominguez Slough, practically an open sewer which drains industrial areas of Los Angeles, Vernon and Torrance inter alia and numerous oil fields. In 11 of 14 checks made during the 1950-1951 survey dissolved oxygen determinations were zero while in the remainder the reading did not go higher than one part per million.

It is notable that in a closeby area (Station B) with very little higher dissolved oxygen (between 2-3 ppm. for much of the year) both Limnoria tripunctata and Teredo diegensis are present. The region of maximal activity (Station D or Zone 6 among the derelict areas) is both close by and highly polluted.

Of the remaining borers of the harbor, Limnoria quadripunctata is found only in Fish Harbor of the zones of heavy pollution. While the major pollution here is of animal origin, lacking the toxicants of Inner Harbor pollution, and while flushing action from the Outer Harbor is probably strong and effective, the fact that this species of Limnoria is a cooler water species probably means that it would not in any case thrive in the warmer waters of the Inner Harbor. Therefore, the observations on distribution in Los Angeles-Long Beach Harbors cannot be taken necessarily to indicate a low tolerance for pollution. For the boring amphipod, Chelura terebrans, the same may be true although we believe that this is a generally less adaptable animal than our two Limnorias. It appears to be restricted to the waters of the Outer Harbor and the Naval Base. Bankia setacea, the larger, coldwater shipworm, has been more difficult to spot as its swimming young (veligers) are released only in the coldest months in our harbor. The one flourishing center we know about is by the lighthouse at the entrance to the breakwater, the coldest area in the harbors. Other centers have been active, but all in cold waters. Therefore, the fact that these are also clean waters may not be significant and one cannot conclude from these observations that Bankia setacea cannot thrive under conditions of pollution.

Council studies of fouling organisms have been carried far enough to show population patterns for the bryozoans, hydroids and tunicates. Of these the hardiest is the small colonial hydroid, Obelia dichotoma, which appears from time to time in small numbers even at Station C where all borers are absent. Like Limnoria tripunctata and Teredo diegensis it flourishes in derelict Zone 6 where industrial toxicants are a little less than maximal.

SUMMARY

1. Surveys of the effects of pollution in Los Angeles-Long Beach Harbors have been made by means of orange-peel bucket sampling of the bottom and by standard block samplers for boring and fouling organisms.

2. Pollution in restricted areas of Los Angeles-Long Beach Harbors has for extended periods reached concentrations stopping all borer and fouling activity.

3. Lethal concentrations for borers have occurred only in parts of the harbor in which tidal flushing appears to be reduced.

4. Bottom life (benthos) appears to be first affected and recovers slowly so that there are large derelict areas about the principal concentrations of pollution.

5. Borers are not equally sensitive to the effects of pollution. Limnoria tripunctata and Teredo diegensis can maintain themselves for considerable periods at concentrations of dissolved oxygen below three parts per million. Limnoria quadripunctata, which thrives in cooler waters, is absent from areas of low dissolved oxygen (high pollution). Chelura terebrans is confined to relatively clean waters. Bankia setacea maintains itself only in the coldest waters so that one gets no conclusive evidence of its relation to the pollution from observations at the isotherms of Los Angeles.

6. Limnoria tripunctata and particularly Teredo diegensis occur in great numbers and increase rapidly in an area of high pollution.

7. Fouling organisms also show a differential sensitivity to pollutants, the hydroid, Obelia dichotoma, appearing to be most hardy.

8. Pollution adequate to check borer and fouling activity completely is paralleled by an accelerated corrosion of harbor equipment.

(Contribution from the Marine Laboratory, University of Miami)

ACCELERATED TEST METHODS OF ANTI-MARINE BORER TREATMENTS

by F. G. Walton Smith

For many years the majority of investigations concerned with the prevention of marine borer attack were of a decidedly empirical nature. Although records of marine borer attack are found in the writings of antiquity, the descriptions of protective methods have consistently sounded like handbooks on witches' caldrons. With few exceptions, only in the present century has a more scientific approach been adopted. Even now the old capricious habit of aimlessly mixing all available unpleasant materials has not been completely abandoned. The results of centuries of empirical tests have shown clearly, however, that no other preservative has ever been found with the effectiveness and long life of pressure-creosote treatment. It was only natural, then, that steps should be taken during the past 30 years to analyze the effects of creosote upon marine borers themselves, to compare a wide range of other toxic compounds with creosote and to attempt to isolate the effective agent in creosote. Experiments of this nature are well summarized in MARINE STRUCTURES, THEIR DETERIORATION AND PRESERVATION published by the National Research Council in 1924.

Unfortunately, experiments of this nature are not sufficient. It is not enough that a preservative should be harmful to an organism immersed in it. There are any number of substances normally found even in a household closet capable of killing marine borers under these conditions. Shipworms will undoubtedly die in a solution of household ammonia, rat poison, sodium pentachlorphenate, or even whiskey and soda. But none of these materials - poisonous though they are - will, when introduced into wood, continue to protect it against the marine borer for considerable periods of time, in the manner that creosote does.

Nevertheless, some kind of a test is necessary and it should preferably be a test of the wood treatment rather than a simple pharmacological test of the preservative independent of the treatment itself. The most direct method, of course, is to impregnate a series of test panels with the compounds under investigation, and to expose them in seawater to marine borer attack. Unfortunately for this method the criterion of success is a treatment which will protect the wood for a period of a good many years. The resultant delay in obtaining controlled experimental data is therefore very considerable. This, in itself, is a serious objection and undoubtedly explains the slow progress which has been made in setting up creosote standards, or in finding acceptable substitutes for creosote.

In the course of the program of marine borer research at Miami, it was early realized that a more rapid test of preservative treatments was necessary and the present report concerns the results of a search for such a test. An interesting parallel to this problem and one which has provided a basis for developing the desirable accelerated test is that which concerns antifouling paints. In this case the problem was to develop a rapid test of

the effective life of such paints. Briefly, most of these paints owe their antifouling properties to the slow solution of a copper compound in seawater. In order to screen the numerous paint formulations an accelerated test method was devised, whereby the copper dissolves at approximately 100 times the average rate in seawater. This test thus provides a roughly quantitative measure of the period over which a paint may be expected to release copper in concentrations sufficient to maintain its antifouling qualities.

In the case of antifouling paints it has been found that increasing the pH of seawater will bring about accelerated leaching of the copper. A similar test for wood preservatives designed to repel marine borers was sought, with its principal objective the testing of preservation by creosote and its chemical and physical fractions. In the initial tests creosote was used to impregnate slips of clear sourthern pine, 1/8 inch in thickness. The impregnation was made by Dr. Sweeney of the Naval Research Laboratory, as part of a cooperative project. A large supply of creosote was purchased in order that a permanent standard could be used for this and all subsequent experiments. This is now referred to, at least informally, as U. S. Experimental Creosote Standard Number 1.

The wooden slips were exposed to various treatments for the purpose of leaching out the preservative in order to simulate the natural loss of preservative under service conditions. By using thin slips of wood it was hoped that leaching would be more rapid. An attempt was made to further accelerate by varying the chemical and physical conditions of the leaching bath.

The initial experiments were carried out in leaching baths at room temperature. Hydrochloric acid and sodium hydroxide were both used to bring about considerable changes in pH of the seawater bath. Other treatments consisted of boiling in seawater and agitation in oxidizing solutions. Controls leached in standing seawater, running seawater and controls with no leaching at all were provided for comparison.

Following the period of leaching, all of the thin wooden slips were immersed in the sea for exposure to marine borers. The results of a typical experiment are shown in Table 1. Boiling in seawater alone was successful in leaching out the active toxicant of the creosote treatment to the point where borer resistance was reduced. Acid, alkali, or oxidizing baths were surprisingly less effective.

These experiments were confirmed by washing leached panels free of the leaching water and placing them in dishes of seawater to which shipworm larvae were added. The results , Table 2, substantially agree with those of the field exposure tests.

Although boiling in seawater was the most effective method of accelerating leaching, it also had the obvious disadvantage that the rates of leaching of the various creosote components might be quite different in the presence of steam than in water below boiling point. Later experiments were there-

TABLE 1

REDUCTION OF PROTECTION AGAINST BORERS AS A RESULT OF LEACHING, AS SHOWN BY FIELD EXPOSURE TESTS[1]

TREATMENT		UN-LEACHED	Boiled in Seawater	Potassium Dichromate	Hydro-chloric Acid	Held in Seawater	Aerated Seawater	Sodium Hydrox-ide
CREOSOTE	Fouling	0	2-3	0	0	0	0	0
	Limnoria	0	0	0	0	0	0	0
	Shipworms	0	1	0	0	0	0	0
UNTREATED	Fouling	4	2	2-3	2	1	2	2
	Limnoria	0	1	1	1	1	1	1
	Shipworms	0	1	2	1	1	2	1

[1] Leaching period 18 days

0 No attack
1 Very light
2 Light
3 Moderate
4 Heavy

TABLE 2

REDUCTION OF ANTI-BORER PROPERTIES BY LEACHING, AS SHOWN BY LABORATORY TEST WITH LARVAE, IN MINUTES

	UNTREATED	CREOSOTED					
Leaching Methods	All Leaching Methods	Aerated Seawater	Hydro-chloric Acid	Sodium Hydroxide	Potassium Dichromate	Held in Seawater	Boiled in Seawater
Exposure which prevents swimming only	Active at 360	115	50	50	50	50	300
Exposure which prevents all motion	Active at 360	115	50	50	50	50	360

fore carried out with water leaching at a temperature of 80°C. The results were similar to those in which boiling seawater was used.

In a later series of experiments a leaching bath was used in which fresh water was maintained at 80°C. with a constant rate of inflow and outflow in order to remove the leached materials. Seven groups of 1/8 inch wooden slips treated with creosote to retention of from 2 to 30 lbs./cubic foot were prepared for this experiment at the Naval Research Laboratory. In each group panels were leached for periods varying from 0 to 48 days, and subsequently exposed to attack in the sea for a period of six months. The results are shown in Table 3. It will be noted that the borer resistance of the treatments decreases progressively with the duration of leaching.

From the data of Table 3, it is clear that a low retention creosote treatment requires less leaching to reduce its anti-borer effectiveness to a predetermined degree than does a high retention treatment. There is thus a definite possibility that the period of leaching required to do this may be used as a rough index of the effective life of the treatment. In order to test this over a long period and for purposes of comparison and calibration, larger (2" x 4") timbers are being exposed to borer attack at the same location at Miami Beach.

From data similar to that of Table 3, leaching ratings were derived for various degrees of creosote retention. The ratings (Table 4) are in terms of the minimum leaching period required to cause light borer attack when subsequently exposed to a 3-months' field exposure.

As an illustration of the possible uses of the leaching test, an assay was made of preservatives developed by the Dow Chemical Company, with the kind permission of Dr. Fred J. Myers. The data are reproduced here in Tables 5 and 6. Table 5 records the results of a leaching test carried out upon seven preservative treatments in a manner similar to that used for the creosote treatments recorded in Table 3. By comparing the data of Table 5 with the "leaching ratings" for the creosote panels, it is possible to rate the Dow treatments in terms of equivalent creosote retentions (Table 6). According to this system of evaluation, the Dow treatment #7 is somewhat superior in service life and effectiveness to a 30 lb. creosote treatment, while #5 and #6 approximate more closely to 20 lb. (15-30) creosote treatment.

It is not yet possible to make any claims for the accelerated leaching test as an index of service life. On the other hand, the experiments conducted so far suggest interesting possibilities and they are therefore being continued in the hope of developing a standard test protocol which will serve to evaluate the probable effectiveness and length of service life of chemical wood borer preventives.

Should such a test method be developed, proven, and calibrated, it should enormously shorten the time needed to evaluate experimental treatments. It should also be of great value in the difficult task of isolating the effective ingredient or ingredients in creosote.

TABLE 3

EFFECTS OF LEACHING IN WATER AT 80°C WITH SUBSEQUENT SIX-MONTH EXPOSURE TO BORER INFECTION (OCT. 15, 1951, TO APRIL 10, 1952)

Days Leached	Control	2 lbs	5 lbs	10 lbs	15 lbs	20 lbs	25 lbs	30 lbs
0	F 5 L 2 S 4	F 2 L 2 S 0-1	F 2 L 2 S 0	F 0 L 2 S 0	F 2 L 0 S 0			
2	F 4 L 4 S 4	F 3 L 3 S 2	F 3 L 4 S 1	F 4 L 1 S 1	F 3 L 2 S 0	F 2 L 2 S 0-1	F 4 L 0 S 0	F 1 L 1 S 0
4	F 4 L 5 S 4	F 3 L 4 S 2	F 4 L 3 S 2	F 4 L 0 S 0-1	F 4 L 1 S 1	F 3 L 0-1 S 0-1	F 3 L 1 S 1	F 2 L 0 S 0
8	Destroyed	F 2 L 5 S 3	F 3 L 5 S 0-1	F 2 L 3 S 1	F 3 L 2 S 0-1	F 4 L 2 S 1	F 3 L 0-1 S 0	F 4 L 1 S 0
16		F 2 L 5 S 2	F 4 L 2-3 S 2	F 3 L 4 S 0-1	F 4 L 2 S 1	F 4 L 2-3 S 0-1	F 4 L 1 S 1	F 3 L 2 S 0-1
34		F 0 L 5 S 2	F 4 L 4 S 3	F 2 L 4 S 1	F 4 L 2 S 2	F 4 L 3 S 0-1	F 4 L 2 S 1	F 4 L 0-1 S 0
48						F 4 L 4 S 0-1	F 4 L 3 S 0-1	F 4 L 3 S 0-1

F - Fouling
L - Limnoria
S - Shipworm

1. very light attack
2. light
3. moderate
4. heavy
5. riddled, very heavy

TABLE 4

MINIMUM LEACHING PERIOD REQUIRED TO CAUSE LIGHT BORER ATTACK IN CREOSOTE PANELS WHEN SUBSEQUENTLY EXPOSED TO 3-MONTH FIELD TESTS

Creosote treatment in lbs./cubic foot	0	2	5	10	15	20	25	30
Leaching period. Days	0	2	2	4	16	16	8	16

TABLE 5

MARINE BORER ATTACK ON DOW CHEMICAL PANELS EXPOSED TO FIELD TEST FOR 3 MONTHS FOLLOWING ACCELERATING TREATMENT IN WATER AT 80°C.

Days Leached	Control	#1	#2	#3	#4	#5	#6	#7
0	F 5 L 2 S 2-3	F 3 L 0 S 0-1	F 2-3 L 0 S 0	F 2-3 L 1-2 S 0	F 2 L 1 S 0-1	F 1 L 0 S 0	F 1 L 0 S 0	F 2-3 L 0-1 S 0-1
2	F 4 L 2 S 1	F 4 L 0-1 S 0-1	F 3-4 L 0 S 0	F 4 L 1 S 1	F 4 L 1 S C-1	F 3 L 0 S 0-1	F 3 L 0 S 0	F 3-4 L 0 S 0-1
4	F 3 L 1 S 2	F 2 L 0-1 S 1	F 3-4 L 1 S 1	F 3 L 1 S 0-1	F 4 L 1 S 0-1	F 4 L 0-1 S 0-1	F 3 L 0 S 0-1	F 3 L 0-1 S 0-1
8	F 3-4 L 2 S 4	F 3 L 0-1 S 0-1	F 3 L 0 S 2	F 4 L 2 S 0-1	F 3 L 1 S 0-1	F 3 L 0 S 0-1	F 2-3 L 0 S 0-1	F 2-3 L 0 S 0-1
16	---	F 2 L 0-1 S 0-1	F 2-3 L 0-1 S 0-1	F 2 L 1 S 0-1	F 2 L 3 S 1	F 1 L 2 S 1	F 2 L 1 S 1	F 1 L 0-1 S 0-1
34	---	---	F 3 L 1 S 1	F 3-4 L 1 S 1	F 3 L 2 S 1	---	F 3 L 2 S 1	F 3 L 1 S 1
48	---	F 2 L 0 S 0-1	F 4 L 0-1 S 0-1	F 3 L 1 S 0-1	F 3-4 L 0 S 0-1	F 3 L 1 S 1	F 4 L 1 S 2	F 3-4 L 1 S 2

TABLE 6

MINIMUM LEACHING PERIOD REQUIRED TO CAUSE LIGHT BORER ATTACK IN DOW PANELS WHEN SUBSEQUENTLY EXPOSED TO 3-MONTH FIELD TESTS

Panel Series	Vehicle	Active Ingredient	Retention lbs./ft.3	Minimum Leaching Period	Equivalent Creosote Treatment in lbs./ft.3
#1	Panalene SN	4% Copper 3-phenyl-salicylate	10 - 12.5	4	10
#2	Panalene SN	4% Copper 3-phenyl-salicylate	20 - 25	4	10
#3	Panalene SN	-	20 - 25	0	0
#4	Dowanol 50B-101E	-	20 - 25	0	0
#5	Dowanol 50B-101E	5% Copper pentachlor-phenate	8 - 10	16	15 - 30
#6	Dowanol 50B-101E	5% Copper pentachlor-phenate	16 - 20	16	15 - 30
#7		2% Copper pentachlor-phenate - ammonia	30 - 40	34	30 plus

(Contribution from the Basic Sciences Research Department, U. S. Naval Civil Engineering Research and Evaluation Laboratory)

FURTHER INVESTIGATION OF INHIBITION OF MARINE BORERS BY TREATING WOOD WITH INSOLUBLE COMPOUNDS OF THE HEAVY METALS

by E. R. Holden and Herbert McKennis, Jr.

In the field of inorganic treatments for the preservation of wood against the destructive activities of marine organisms, two groups of compounds, the various forms of iron oxides and the sulfides of certain heavy metals, are of special interest. The potential usefulness of the iron compounds is based primarily on the known fact that rusting iron nails afford effective protection to wood (1,2). The second group of compounds, the heavy metal sulfides, have been selected as a subject of investigation because of the known toxicity of the compounds of the particular metals, the extremely low solubilities of the sulfides, and their probable resistance toward losses through oxidation processes.

In general, the wood is impregnated with a solution of a soluble salt and then treated with a second material to precipitate an insoluble heavy metal compound. The natural resins have been observed to exert an influence on, and sometimes appear to prohibit, these reactions. In an effort to circumvent such difficulties, as arise from participation of wood, chemically or physically in these reactions, different methods and reactants which normally produce the same desired compound have been used. Pertinent basic studies relative to compound formation are being conducted also, so as to provide essential information for the performance tests.

The standard test block for panels which are placed in harbor water is 2" x 4" x 12" in size. In some cases splints approximately $2\frac{1}{2}$" x 2" x $\frac{1}{4}$" are treated simultaneously for use in a cooperative program wherein accelerated tests (3) are being conducted at the Marine Laboratory, University of Miami, under the direction of Dr. F. G. Walton Smith. For a given treatment, nine blocks (2" x 4" x 12") are placed in the water in order that blocks may be removed after intervals of time for internal inspection without terminating the test.

IRON OXIDES

There are seven important allotropic forms of ferric oxide: α-, β-, and γ-monohydrates, the corresponding anhydrous α- and γ- forms, the hydrous oxide[1], and magnetite (considering magnetite to be a double oxide of ferric and ferrous oxides in approximately equimolar ratio). In the normal "rusting" or slow oxidation of iron gradual step changes are believed to occur with

[1]The "hydrous oxide" may be, actually, a hydrozide (6).

the following substances formed successively: Ferrous hydroxide ⟶ ferrous oxide ⟶ magnetite ⟶ γ-ferric oxide monohydrate ⟶ α-ferric oxide monohydrate. There may very well be departures from this schematic arrangement, but under the conditions with which this work is concerned, the limited oxygen supply and the 7.4 - 8.5 pH range of sea water (4) would be expected to favor this mode of chemical change. In X-ray diffraction studies made by Mr. T. L. Starr of this Laboratory the major ultimate product was identified as the α-monohydrate in scrapings taken from iron nails which had been immersed in sea water for several months (see Figure 1a). This being known, it would be very desirable to precipitate this form in the wood for test purposes, but unfortunately, the information available concerning its synthesis is insufficient to devise a method to accomplish such treatment with certainty. However, it has been possible to precipitate the intermediates in wood which may very well achieve the same purpose. The transformation of the intermediates to the ultimate condition of form and particle size may be somewhat slow because of the small energy differences (5) and low solubilities. An effort has been made to form all the other types in wood, as well, in order that the investigation be as complete as possible.

Hydrous ferric oxide (Hydrous Fe_2O_3 or $Fe(OH)_3$)

In the first tests made a ferric salt was precipitated by ammonium hydroxide in wood. The protection afforded by this particular treatment was insufficient to be of practical value. This method precipitates a hydrophilic sol usually referred to as "hydrous ferric oxide." The particles are too small to give an X-ray diffraction pattern until aged for many months at room temperature. The aged gel produces the anhydrous α-ferric oxide X-ray diffraction pattern. Prior to this change the hydrous oxide is much more soluble and readily subject to colloidal dispersion and, therefore, may very well undergo serious leaching. Phase rule studies by Weiser and Milligan (6) indicate that the initial form is a simple oxide or hydroxide, and the eventual product, as mentioned above, is the anhydrous α-form, both forms being very different from that identified in rust scrapings both as to crystal type and particle size.

Anhydrous α-ferric oxide (α-Fe_2O_3)

The conversion of the hydrous ferric oxide gel to the anhydrous α-form takes place rapidly at 600°C. or above. The product is a fine, very hard, brick red crystalline material identical to mineral hematite and commercial red rouge. It was found that this conversion temperature could be lowered to 120°C. by use of saturated steam (15 psi) which is known to reduce the temperature required in the dehydration of this as well as many similar hydrates. Under these conditions this transition would involve a time-pressure relationship in which pressure is a parameter of temperature, and it is possible that the change would take place rapidly at a slightly lower pressure. However it could not be reduced to as low as atmospheric pressure, because the boiling of a suspension has been found to be very slow in bringing about the conversion to particles large enough to produce

X-ray diffraction patterns. Since this temperature is low enough to avoid serious thermal decomposition or structural alteration of wood an effort was made to form the compound directly in wood. Southern yellow pine blocks were impregnated with 10% ferric chloride, treated with ammonia and heat treated in an autoclave for a period of six hours. The wood became dark brown, presumably because of the formation of iron resinate. These blocks are now being studied for marine borer resistance. Currently no method is available for confirming the presence of the oxide normally obtained by this method.

β-ferric oxide monohydrate (β-FeOOH)

When ferric chloride solutions are heated to 80-100°C. an orange-yellow substance precipitates from solutions, which is considered, generally, to be an allotropic form of ferric oxide monohydrate and designated as the β-form. This same material sometimes forms gradually in ferric chloride solutions when permitted to stand for long periods of time. X-ray diffraction patterns show that this substance has a crystalline structure which is distinctly different from the other oxides. Some question still exists regarding its true structure, since it always contains a large amount of chloride that may be leached out extensively without detectible change in X-ray diffraction pattern. When the β-form is dehydrated by heat treatment, it changes to the anhydrous α-form without any known intermediate.

An attempt was made to treat blocks in such manner as would cause the formation of this oxide in wood. Blocks were impregnated with a 10% ferric chloride solution by means of the vacuum-pressure method and subsequently heated to 80°C. for several hours while immersed in the same solution. The ferric chloride did not form a precipitate in this case at all. This failure is attributed to the reaction of ferric chloride with the resinous acids in the wood. It was apparent that a considerable amount of the resins had steeped from the wood, in that an appreciable quantity of a gummy material remained as a residue when the solution was concentrated subsequently. This occurrence is to be expected, since the temperature used is above the softening point of the resins. It is suggested, as explanation for the interference in the oxide formation, that much of the ferric chloride reacted with the resin in a manner such as is shown by the following equation, which is, admittedly, an over-simplification: ferric chloride + resinous acids $\longrightarrow$ ferric resinated + hydrocloric acid. The formation of ferric resinate would decrease the ferric ion concentration markedly inasmuch as it is fairly insoluble and the compound remaining in solution would be largely undissociated. Though there is no evidence that the β-form was actually obtained in the wood, the treatment had some definite effect on the constitution of the wood and for this reason the blocks were placed in the sea to determine their performance. It is possible that some modifications in this method may be found so as to obtain suitable results. It is a further possibility that some types of wood other than the southern yellow pine used in these experiments might not contain such prohibitive amounts of interfering substances.

γ-ferric oxide monohydrate (γ-FeOOH) and magnetite (Fe_3O_4 or $Fe_2O_3 \cdot FeO$)

Synthetic γ-ferric oxide monohydrate is orange-yellow in color as a powder, and is identical to the mineral lepidocrocite.[1] It may be dehydrated to an anhydrous γ-form by heating to about 250°C. At higher temperatures the anhydrous form reverts to the α-oxide, as do other varieties.

Since the γ-monohydrate is regarded as an intermediate substance in the gradual oxidation of metallic iron to the final product, the α-monohydrate, somewhat greater effort has been made to find a suitable way to form this material in wood. This presents difficulties, because of inadequacies in the basic knowledge relative to the synthesis of this particular form.

Fairly pure γ-monohydrate can be made by oxidizing the precipitate formed on the addition of pyridine to ferrous chloride, as described by Baudisch and Albrecht (7), or by the oxidation of magnetite. While these authors acknowledge that the γ-form can be made using certain other ferrous compounds (1,10), they stated that, ". . . it was impossible to obtain the γ-hydrate from ferrous sulfate . . .," and, generally, describe the essential condition under which the reaction may take place as being dependent on the tendency of the reactants to form complexes. In our work we have found it possible to obtain the γ-form from ferrous sulfate, and have made some study of the variations in the hydrogen ion concentration during reaction periods and their influence on the kind of reaction products obtained.

In general, when a basic substance is added to a ferrous salt, a white film-like precipitate forms at first that degenerates to a green and finally to a black material. When this precipitate is oxidized usually a mixture of the α- and γ-ferric oxide monohydrates is obtained. Prior to oxidation, the suspended particles produce a higher pH value than that of the surroundihg solution, which is primarily the excess of the ferrous salt used, as shown by the data in Table 1. In using a glass electrode pH meter, it was found necessary to take very rapid readings in order to obtain meaningful values because these suspended particles tended to collect rapidly on the surface of the electrodes causing an instrumental drift and thus yielding values other than an "average" pH for the true solution plus the colloidal phase. The electrodes were rinsed between each measurement to eliminate any accumulative change. While this did not remove adhering particles, it apparently allowed the film to oxidize, so as not to affect the calibration of the instrument. The reproducibility of the values obtained with this procedure was within the approximate limits of 0.1 pH. In the above tests it was observed that after the addition of sodium hydroxide to a ferrous sulfate solution the pH did not immediately assume a constant value. The initial reading was the highest value attained from which successive readings would gradually decrease. Table 2 shows the changes in pH when 7.5 cc. of 1M. sodium hydroxide were added to 100 cc. of 0.5 M. ferrous sulfate, with air bubbling through the solution to cause oxidation

[1] Lepidocrocite is a pleochroic mineral exhibiting several colors, depending on the surface viewed. Naturally-occurring crystals which are probably larger appear as blood red (7).

of the precipitate. Also shown are the pH values obtained simultaneously for the same ingredients not aerated and surface oxidation minimized by a stream of nitrogen in a covered vessel which was opened only when pH readings were taken. The data suggest that the particles in suspension when first formed are hydroxides of some type, such as ferrous hydroxide, and give rise to a pH value higher than that of the surrounding true solution, as mentioned above, and slowly change to the oxide by the spontaneous loss of water to form the theoretical anhydride as represented empirically in the equation:

$$Fe(OH)_2 \rightarrow FeO + H_2O$$

After the pH of the unaerated sample dropped from 6.1 to 4.7 in the first hour and 45 minutes, the readings taken in the next 18 hours remained the same. This would indicate that the above possible reaction is reversible and that it gradually establishes equilibrium on standing, at pH of 4.7 in this particular case. It has been observed that the precipitate is much more readily oxidized when first formed. Thus it is postulated that the hydroxide is oxidized rather than the corresponding oxide. There are additional reasons for believing this to be the case. It is known that magnetite is more easily oxidized in strongly alkaline solutions (11), and the slow drop in pH below 4.7 (20 to 30 hrs.) of the aerated sample before reaching an equilibrium value also indicates this.

When the pH of the aerated sample became lower than 4.6, the instrument drift reversed, tending to give lower readings as particles coalesced on the electrodes. This value coincides with the equilibrium value reached by the sample not exposed to oxidizing conditions. Possibly this is related to selective adsorption involving "ferrous acid" ($HFeO_2$ or $FeOOH$) with very high total surface area in the early stages of precipitation. However, more experimental work will be necessary before adequate explanation can be made as to the unusual reversal.

When ferrous sulfate was treated with an excess of ammonium hydroxide and aerated for a period of 72 hours, magnetite was the predominant product, as shown by its strong ferromagnetic property, black color, and X-ray diffraction pattern. A second sample was prepared similarly, but was permitted to stand 24 hours, filtered to remove the soluble portions and then allowed to aerate for a period of 24 hours while suspended in distilled water. The oxide in this case was found to be mainly the γ-monohydrate as shown by X-ray diffraction patterns and ferromagnetic behavior of a portion dehydrated at a temperature of 250°C. A third sample was prepared by adding small portions of ammonium hydroxide to ferrous sulfate and oxidizing the precipitate while under acid conditions. This sample was found to contain the γ-form, but tests showed that it was less pure. From these results it appeared that the γ-form was obtained at a pH of about 6 to 7 and that a contaminating substance was formed at a lower pH value. As already described, exact control of pH for this heterogeneous system is difficult but it appeared desirable to make further tests regulating the pH, i.e., the average value, as well as possible. This was done by titrating 0.5M. $FeSO_4$ with 1M. NaOH at such rate as would

maintain a given pH range. Samples held near a pH of 7 produced nearly pure γ-monohydrate, while those restricted to a pH of 4.5 or less produced mainly the α-form (see X-ray diffraction patterns b and c in Figure 1). Further work is contemplated along these lines so as to permit more exact delineation of the conditions for the formation of these oxides.

Wood blocks have been treated variously by vacuum-pressure and steeping methods using ferrous sulfate in the first treatment and ammonia, ammonium hydroxide, or pyridine in the second. It is not possible to determine what specific forms are actually obtained in these treatments, but it is reasonable to assume that they will consist of the oxides of a definite group, namely, magnetite and α- and γ-monohydrates. It is hoped that the use of different methods will affect the final product and thereby obtain differences which may affect their performance. The physical state of the oxides should be eventually like that of rust from metallic iron, since these forms are considered to be either intermediate in the oxidation of iron or the same as the ultimate product.

HEAVY METAL SULFIDES

Compounds of the heavy metals are well established as being toxic to animal life and are known to produce important physiological effects in trace amounts. Copper sulfate, for example, is widely used as an economic poison in the control of a large number of species in the general biological groups, mollusks and arthropods, to which the various species of marine borers belong. This compound is an effective molluscacide in very low concentrations, and is currently in large scale use for this purpose (12), in canals and similar constricted bodies of water. But this particular compound would not be suitable for the preservation of marine timbers because it would be rapidly lost through the serious leaching action of the sea. The sulfides of copper and other like metals are, however, extremely insoluble and, therefore, it is conceivable that they may be useful in this capacity. The sulfides included in the present test program are those of copper, lead, mercury, nickel, zinc, cadmium, iron and silver.

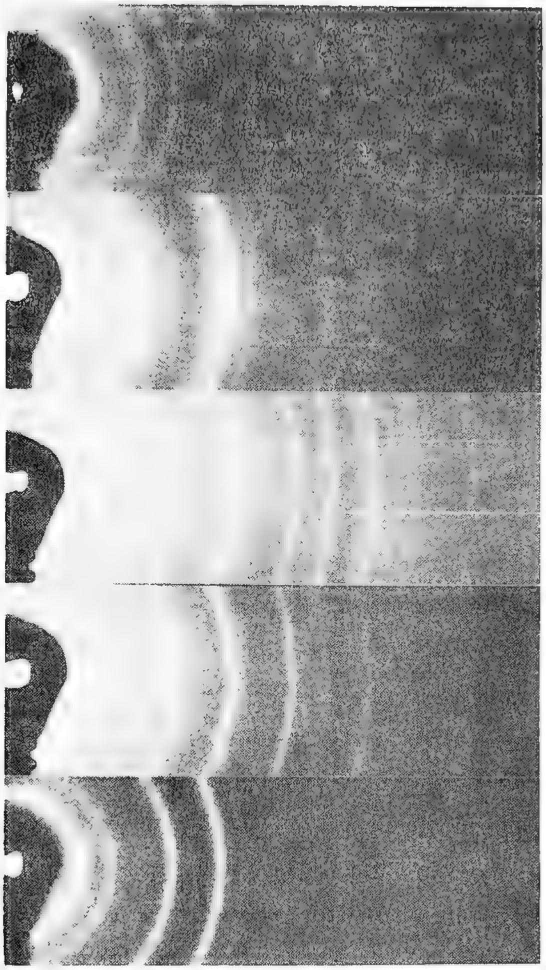
The particle size of copper sulfide varies with different methods of precipitation. Observations as to the nature of the suspensions and microscopic examinations of the powders show that the following methods produce particles of decreasing size in the order listed.

(1) Heat treatment of equal parts of 5% copper sulfate and 12% sodium thiosulfate.

(2) 2.5% copper sulfate, plus hydrogen sulfide.

(3) Equal parts of 2.5% copper sulfate and 2.5% ammonium sulfide.

When blocks were impregnated with solutions of method (1) above and heat treated, the procedure used by Ramage and Burd (13), the wood became a greenish-gray in color, but judging by the color the actual amount of



a. Nail scrapings
α-hydrate

b. "Avg." pH < 4.5
α-hydrate

c. "Avg." pH 6 - 7
Primarily γ-hydrate

d. γ-hydrate
(Baudisch)

e. β-hydrate (from ferric chloride)

Fig. 1 Ferric oxide monohydrates X-ray diffraction patterns identifying the rust on iron nails as the α-form and showing the effect of the "average" pH range on the form obtained in the oxidation of a ferrous precipitate. Pure γ- and β- forms are shown also as (d) and (e) respectively.

copper sulfide formed by the reaction did not appear to be very great. Since the influence of the wood and its natural resins is not readily amenable to control, the sulfides have been precipitated in the wood by several procedures using both hydrogen sulfide and ammonium sulfide in an effort to fully test their relative merits.

Solubilities of Metal Sulfides

The solubilities of the sulfides in pure water as calculated by Kolthoff (14) and Ravitz (15) are given in Table 3. The most important factor affecting the solubility of a sulfide is the hydrogen ion concentration, the solubility being proportional to the square of this value. Since the pH of sea water is usually greater than 7 this would favor even lower solubilities than in pure water. The solubilities should be of the same order of magnitude, though they may be actually somewhat greater than in pure water because of the solvent action of the salts in sea water.

Performance Tests

While large numbers of treated blocks are now in the water it is too early to make any appraisal of their durability with the exception of copper sulfide. The blocks with a surface treatment having a maximum penetration of about 1/8 of an inch were unattacked in the first year at Port Hueneme but are being infected now near the end of the second year. Uniformly treated blocks are now in the water along with the various other metal sulfide treatments for better evaluation of the protective value.

SUMMARY AND CONCLUSIONS

Studies have been made of the chemical and physical properties of the various forms of iron oxide and the metal sulfides relative to their usefulness as wood preservatives.

It has been possible to impregnate wood with certain forms of iron oxide that are believed to be intermediates in the normal oxidation of metallic iron under sea water conditions. The experimental findings as to the conditions affecting the formation of these oxides have been as follows:

(1) The γ-ferric oxide monohydrate can be obtained by oxidation of the precipitate resulting from the addition of either ammonium or sodium hydroxide to ferrous sulfate when the rate at which the hydroxide is added is regulated by means of the pH value for the heterogeneous mixture.

(2) The precipitation of a ferrous salt by a base produces particles which have a higher pH reaction than the solution in which they are suspended.

(3) The particles formed under conditions of item (2) undergo a spontaneous change during the first two hours or so accompanied by a decrease in average pH value (true solution, plus suspended particles) to an equilibrium condition intermediate to that of the original solution and the maximum pH attained on the addition of the hydroxide.

(4) The initially precipitated ferrous material is much more readily oxidized than the alteration product described in item (3).

(5) The concentration of the hydrogen and/or hydroxyl ions has an important influence on the type of oxide formed from a ferrous salt, magnetite being favored in basic solutions, γ-ferric oxide monohydrate in solutions near the neutral point, and α-ferric oxide monohydrate in more acid solutions.

The natural resins in southern yellow pine have been found to interfere with the formation of some compounds. β-ferric oxide was apparently not formed at all and the conversion of the hydrous gel to the anhydrous α-ferric oxide was doubtful. Similarly, it is believed that copper sulfide may not be very efficiently formed in the wood through interaction of copper sulfate and sodium thiosulfate when heat treated.

ACKNOWLEDGMENT

The authors are indebted to Mr. W. L. Starr and Mr. A. I. Funai for the extensive X-ray diffraction analyses made in these studies.

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Table 1. Effect of precipitate formed by the addition of 8.5 cc. 1M. NaOH to 200 cc. 0.5 M. $FeSO_4$ on pH after aging 20 hours at room temperature.

Solution	pH: Filtered after aging	pH: Filtered before aging
$FeSO_4$ with precipitate in suspension	5.5	--
$FeSO_4$ after most of precipitate was removed	4.5	3.4
Precipitate in water suspension	6.1	5.1

* * * * * * *

Table 2. pH change with time for a solution containing 100 cc. 0.5 M. $FeSO_4$ and 7.5 cc. 1 M. NaOH. Column 2 shows result when air is bubbled through solution, and Column 3 shows when solution is protected from air by a stream of nitrogen. Each was agitated and readings were taken quickly to minimize instrument drift.

Time hrs:min	pH: Air	pH: Nitrogen	pH: Diff.
0:03	6.1	6.1	0.0
0:15	5.6	5.8	0.2
0:30	4.9	5.4	0.5
0:45	4.8	5.2	0.4
1:00	4.7	5.1	0.4
1:15	4.1	4.9	0.8
1:30	4.0	4.8	0.8
1:45	3.9	4.7	0.8
2:20	3.7	4.7	1.0
2:50	3.4	4.7	1.3
20:00	2.8	4.7	1.9
30:00	2.7	--	--

Table 3. Solubilities of the heavy metal sulfides.

Sulfide	Temperature	Solubility moles/liter of water	Calculated by
ZnS	25°	$1.47 \times 10^{-9.0}$	Ravitz
PbS	25	$3.62 \times 10^{-11.0}$	"
CuS	25	$2.55 \times 10^{-15.0}$	"
Cu_2S	25	$1.19 \times 10^{-14.0}$	"
Ag_2S	25	$2.48 \times 10^{-15.0}$	"
CdS	25	$1.46 \times 10^{-10.0}$	"
FeS	(*)	$1 \times 10^{-16.8}$	Kolthoff
CoS	(*)	$1 \times 10^{-9.3}$	"
NiS	(*)	$1 \times 10^{-9.4}$	"
Hg_2S	(*)	$1 \times 10^{-19.4}$	"
HgS	(*)	$1 \times 10^{-22.7}$	"

*Presumed to be at or near room temperature.

(Contribution from the Marine Laboratory, University of Miami)

RESPIRATION OF *TEREDO* LARVAE

by Charles E. Lane

Previous communications from this laboratory (Lane, Posner & Greenfield, 1952, Lasker and Lane 1953, and Isham and Tierney 1953) have shown that the free-swimming, infective larval stage of *Teredo* in local waters does not significantly exceed seventy-two hours in extent. During this time the animals have not been observed to feed. The pre-attachment activities of the animal must be presumed to be powered chiefly by glycogen. This is deposited in the ovum in granular form during oögenesis. Additional glycogen may be contributed to the larva during the time that it is actually embedded in the maternal gill (Lane, Posner & Greenfield *loc cit*). At the termination of this transient free-swimming stage the larvae attach themselves permanently to a wooden substratum within which they spend the rest of their adult life span. A cellulase enzyme system exists in both larval and adult *Teredo* (Greenfield and Lane, 1953). This enzyme complex may contribute significantly to the process of penetration of the wood.

The act of penetration of wood confers upon the larva a degree of immunity to environmental hazards except those in solution -- either in the wood itself or in the water which constitutes the respiratory stream. Thus it is that preventive measures, to be effective, must be directed against the larva during the vulnerable first seventy-two hours of its life.

A sensitive index of physiological condition, or of the effectiveness of sub-lethal concentrations of toxic substances, is provided by the rate of oxygen consumption of living systems. Thus it became of interest to delimit some of the parameters of normal respiration in the free-living, pre-attachment stages of our local *Teredo* before beginning any study of the effectiveness of toxic materials. It is the purpose of this communication briefly to describe the methods and some of the results of this study of normal animals.

The apparatus employed is a capillary microrespirometer, Fig. 1. It consists of a pear-shaped chamber blown in one end of 0.5 mm. pyrex capillary tubing. The volume of the chamber varied in different respirometers over the range of six to 125 microliters ($1 \mu L = 1 mm^3$). The volume should be kept as small as possible to increase the stability of the system (Tobias 1943). At the other end of the capillary tubing is an inside syringe-taper ground joint. This seats in the outer matching ground joint of the thermobarometer or compensation chamber. This latter portion of the apparatus should be as large as is consistent with ease of manipulation. We have generally sought to have its volume 1000 times that of the respirometer chamber. This insures maximum sensitivity of the system. The upper end of the compensation chamber is closed by a stopcock. The entire assembly is immersed in a constant temperature water bath maintained at 25.0°C.

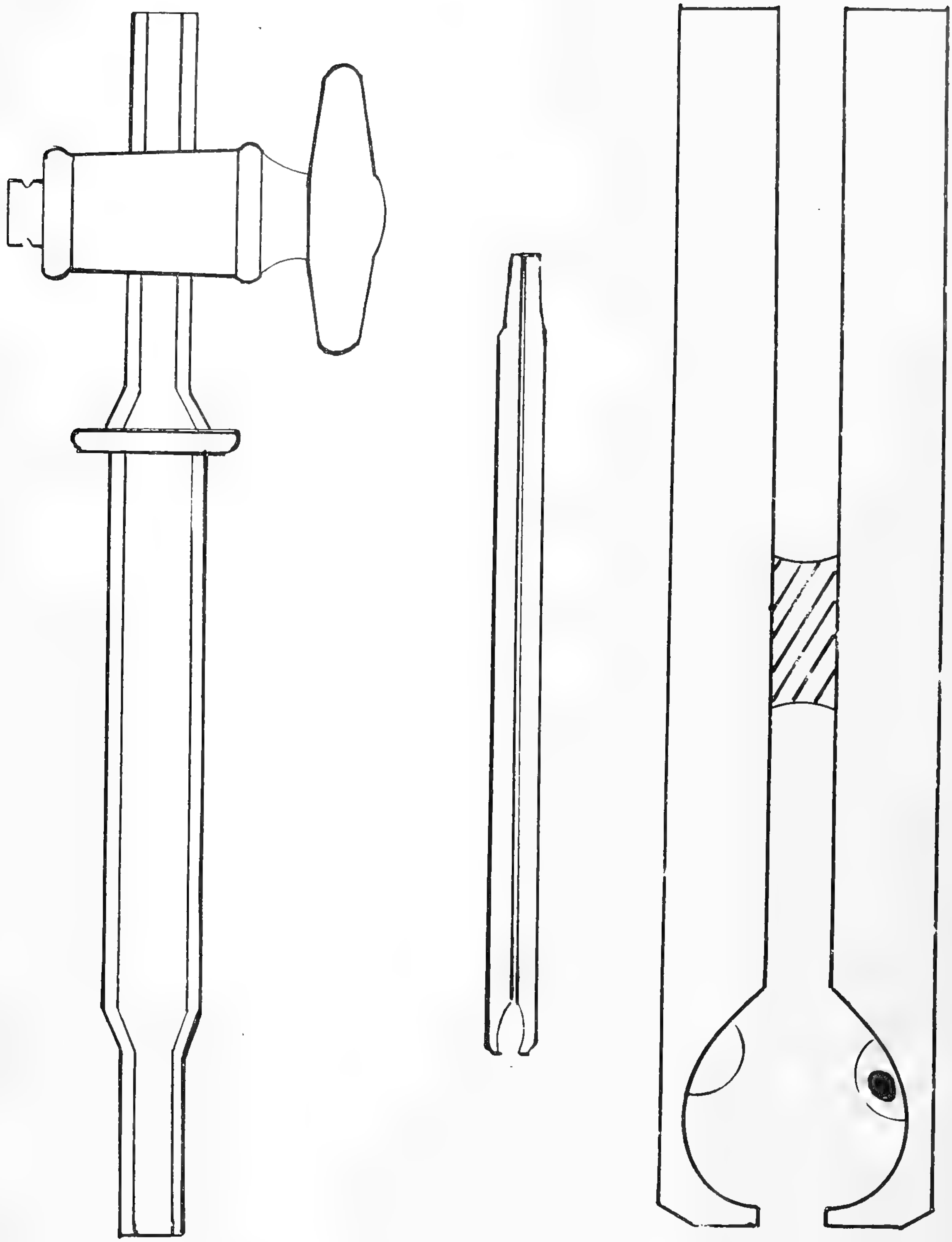

Fig. 1. Sketch of capillary microrespirometer components. Inset shows the respirometer changer with the droplet of medium and a contained larva.

In use the chamber is first charged with a single animal confined in 20 microliters of medium. This isolation and determination of volume of the medium can be effected most easily by making use of specially drawn micropipettes, actuated by a mouthpiece similar to that of a hemocytometer pipette. The loading pipette is calibrated to deliver 20 microliters. This droplet is delivered onto one wall of the respirometer chamber. The chamber wall is previously rendered hydrophobic by the application of a silicone coating, such as "Dessicote" or "Nalcote." Under these conditions the droplet of medium and its contained larva will retain its integrity over long periods of time. It has, for example, frequently been possible to make observations on a single larva during periods as long as twenty-four hours.

After the respirometer has been charged with the animal and its medium, a droplet containing ten microliters of alkali, either 10% NaOH or 10% $Ba(OH)_2$, is placed on the contralateral wall. A droplet of highly purified kerosene is placed in the capillary portion of the respirometer; the open end of the respirometer is sealed with a non-oxidizing wax. For best adhesion and complete sealing it is preferable to employ a wax of low melting point. With the upper stopcock of the compensation chamber open the two portions of the apparatus are united, seated and the joint is sealed with the same wax which was used to close the lower end of the respirometer. The assembly is then placed in the water bath and permitted to come to temperature equilibrium. Empty respirometers generally reach a steady state within thirty minutes.

Our first concern was to determine the extent of the respiratory changes which occur during normal development and maturation of free-swimming larvae. Average results, secured from a study of 115 larval Teredo are shown in Fig. 2. It will be observed that there is a real, and statistically significant, increase in oxygen consumption during the first twenty-four hours of development. Thereafter for the remainder of the normally infective, seventy-two hour period the rate of oxygen consumption drops abruptly and steadily. It may be recalled that Isham and Tierney (loc.cit.) denied larval T. pedicellata access to wood and found that after seventy-two hours involutional changes were initiated which terminated in death of all such forms by the end of three hundred hours. Our respiratory data supplement and confirm these observations. After seventy-two hours the curve of oxygen uptake shows a steady decline. It should also be recalled that larval Teredo have not been observed to ingest solid food; they are provided with a finite glycogen store from the maternal organism. Decrease in voluntary activity, in oxygen uptake and in glycogen content are all related phenomena.

A small series of ten 24-hour larvae was studied in which the sea water medium was made 0.001 M with glucose. These results are summarized in Fig. 3. It will be observed that the addition of glucose to the medium resulted in a 43% increase in the rate of oxygen uptake. This must signify that dissolved nutrient materials may be extracted from the medium, even though the ingestion of solid food has not been observed.

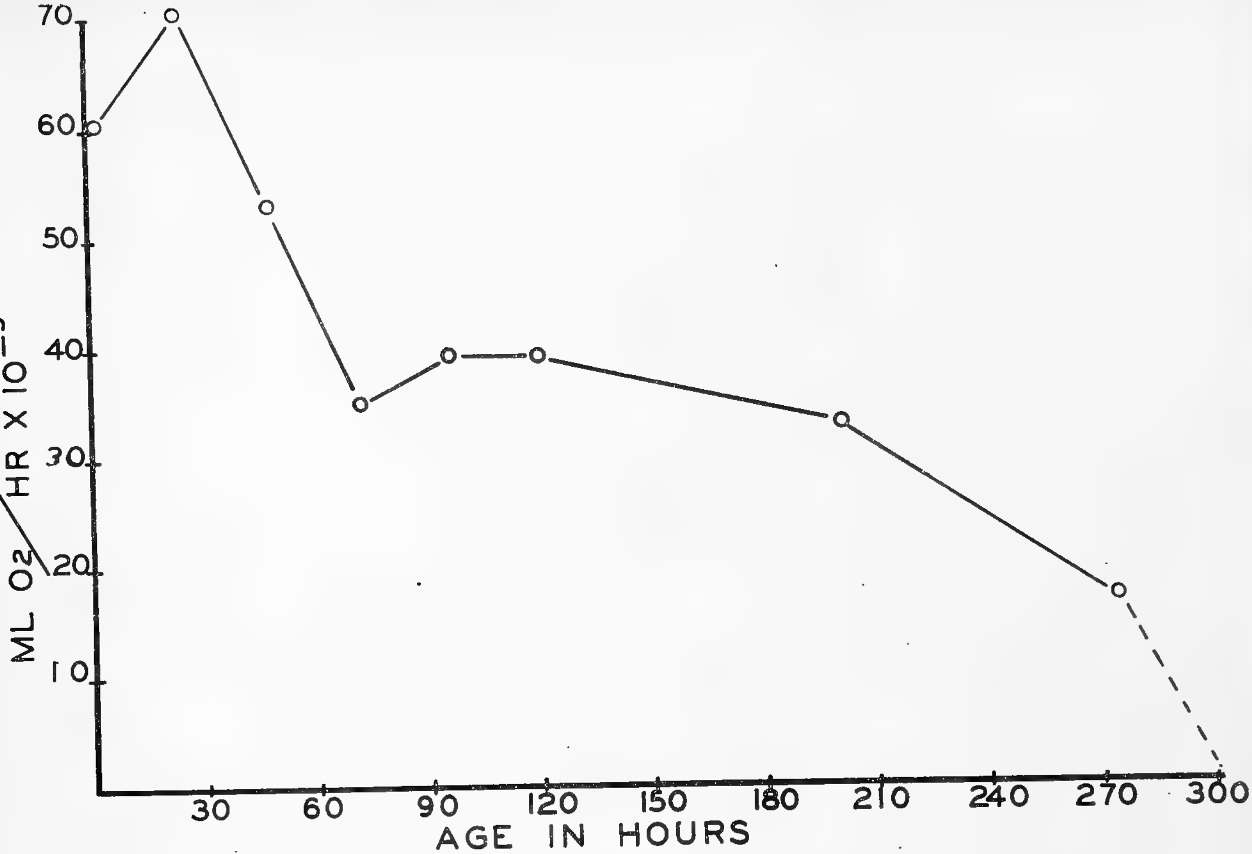

Fig. 2. Oxygen consumption vs. age in larvae of <u>Teredo</u>. Each plotted point is the average of all observations.

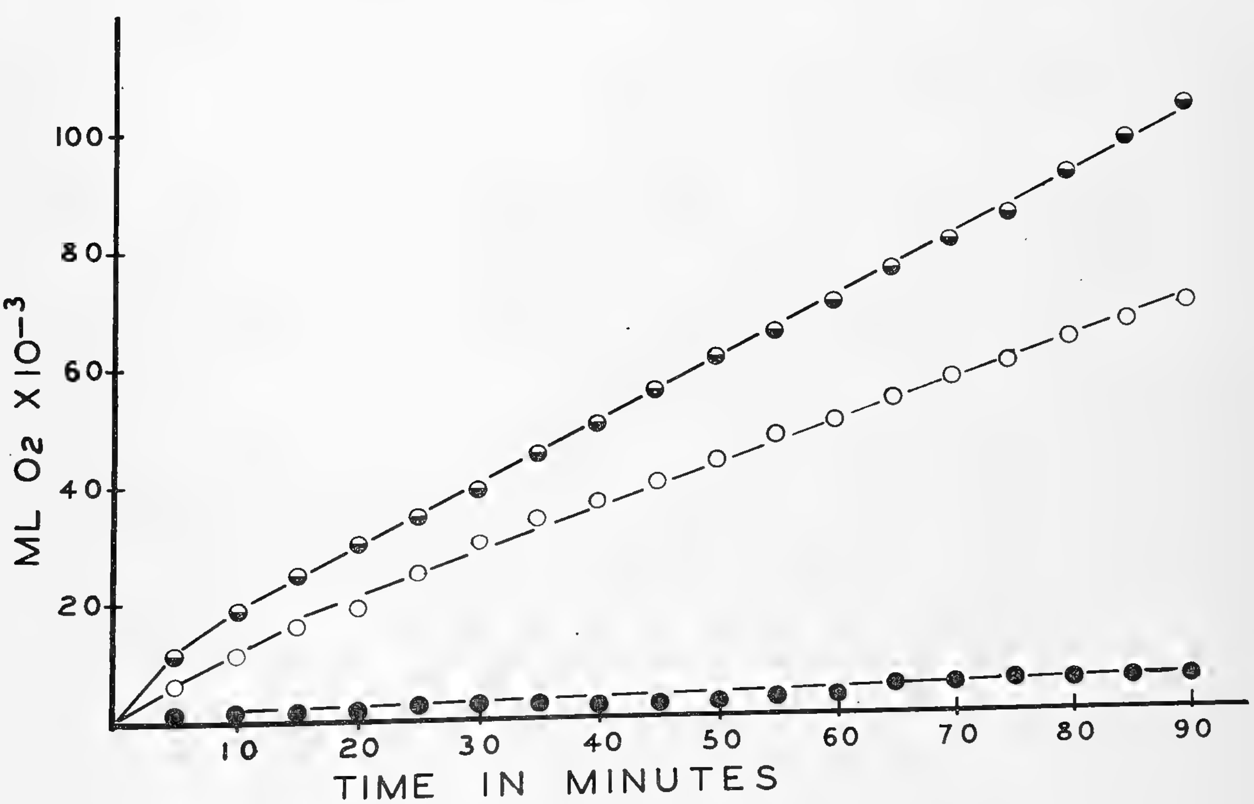

Fig. 3. Average oxygen consumption rates during a ninety minute run of the respirometer. The lowest curve represents oxygen uptake by the sea water medium alone. The middle curve depicts the average oxygen uptake by normal twenty-four hour larvae. The uppermost curve shows the effect of 0.001M glucose on the respiration of normal twenty-four hour larvae.

Using the data for the normal respiratory metabolism of Teredo larvae as a standard of comparison a beginning has been made in a study of the toxicity of whole, crude creosote. Known amounts of creosote were homogenized with sea water in a hand homogenizer. Aliquots of the initial homogenate were then further diluted and homogenized with sea water. It was found that a concentration of 0.5×10^{-9} gm/ml produced approximately fifty percent reduction in oxygen consumption. 0.5×10^{-6} gm/ml killed all the larvae tested within three hours.

In summary then, a method has been presented which permits the determination of oxygen consumption by a single Teredo larva. Results have been presented which detail the oxygen consumption of larvae at different stages of their free-living existence. Evidence has been presented which suggests that Teredo larvae may absorb dissolved nutrient materials from their medium. Finally creosote has been shown to effect a fifty percent decrease in oxygen uptake by twenty-four hour larvae when it is employed in a concentration of 0.5×10^{-9} gm/ml of medium.

Further details and clarifying observations will appear in appropriate technical journals.

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(Contribution from William F. Clapp Laboratories, Inc.)

THE USE OF CHLORINATION AND HEAT IN THE CONTROL OF MARINE BORERS.

by Albert P. Richards

A very definite problem has existed for some time in regard to the activities of marine organisms, both the so-called fouling organisms and marine borers, in more or less confined areas containing sea water. These environments take such forms as sea water intake tunnels of metal or concrete, storage tanks, the interior of drydock pontoons, etc. The attachment of quantities of organisms to the walls of sea water conduits in many locations results in considerable economic loss due to the reduction of flow of water, especially where the water capacity is needed for efficient plant operation. In the case of one power-generating station on the North Atlantic seaboard, having a concrete condenser cooling water intake tunnel approximately 7 feet square and 250 feet long, 331 tons of mussels, *Mytilus edulis*, were removed, having accumulated from June to November of one year. Naturally the volume of these organisms reduced the effective cross section of the tunnel to a point where the flow of cooling water was not sufficient to meet the requirements. It is also interesting to note that the conditions in the tunnel were such that abnormal growth rates of *Mytilus edulis* were recorded. Studies made at the time of annual cleanings at this site indicated a rate of growth of at least 1000 tons per acre per year, while the best yeild from crop farms for this organism under favorable conditions are of the order of 10 tons per acre per year. Similar conditions having been encountered at many locations, it is logical that a considerable amount of research has been carried out in an effort to develop methods of control. Two such methods which show considerable promise in this field involve (1) the chlorination of the sea water, and (2) the use of elevated temperature. A number of commercial installations using one or the other of these methods are now in operation. Due to the fact that in numerous instances analogous situations exist in which marine borers are encountered, it was only natural that during the course of the above mentioned work the reactions of the boring organisms to heat and chlorine were also studied.

It must be remembered that the actual values mentioned in the following discussions must be regarded, not as absolute quantities, but rather in a general way since the species covered specific location of the test, etc., all exert a considerable influence on the results obtained. Actually, any close limits must be determined under the expected conditions of service. The work is still in progress and much remains to be learned.

A large proportion of the laboratory studies was carried out at the International Nicket Company marine exposure laboratory at Wrightsville Beach, North Carolina through the courtesy and cooperation of Mr. LaQue and Mr. H. T. Paterson of that company, and Mr. R. B. Martin of the Wallace & Tiernan Products Inc. who supplied much apparatus and valuable help.

Two experimental assemblies were constructed, the first for hot water studies consists of three water lines supplying continuously flowing sea water to individual weir boxes. One of the lines furnishes normal sea water as a control and provision is made to raise the temperature of the water in the other two lines to a selected point on any time schedule desired. The samples under investigation are placed in the weir boxes during the test runs.

The second assembly consists of eight lines supplying identical weir boxes with water which may individually be chlorinated to selected residual concentrations of chlorine by eight automatic feeders on predetermined schedules. Provision has also been made to introduce temperature changes as well as chlorination.

During the summer of 1950 the effect of rather broad residuals of chlorine on the teredine borers was studied. Future reference to chlorine concentrations in these remarks will refer to residuals.

The following concentrations were established in the eight weir boxes, the test pieces being 2"x4"x4" wooden blocks:

1. Control
2. Continuous chlorination at 0.25 ppm
3. Continuous chlorination at 0.50 ppm
4. Intermittent chlorination at 1.5 ppm, 2 hours on, 4 hours off.
5. Intermittent chlorination at 3.0 ppm, 2 hours on, 4 hours off.
6. Intermittent chlorination at 1.5 ppm, 2 hours on, 2 hours off.
7. Intermittent chlorination at 3.0 ppm, 2 hours on, 2 hours off.
8. Intermittent chlorination at 0.5 ppm, 2 weeks on, 2 weeks off.

This series commenced on July 31st and was terminated on September 29th with the results of the final inspection of the blocks as follows:

#1 - Control, 200± Teredinidae

#2 - Continuous .25 ppm - no borers.

#3 - Continuous .50 ppm - no borers.

#4 - Intermittent 1.5 ppm, 2 hrs. on, 4 hrs. off - 50± Teredinidae.

#5 - Intermittent 3.0 ppm, 2 hrs. on, 4 hrs. off - no borers.

#6 - Intermittent 1.5 ppm, 2 hrs. on, 2 hrs. off - no borers.

#7 - Intermittent 3.0 ppm, 2 hrs. on, 2 hrs. off - no borers.

#8 - Intermittent .5 ppm, 2 weeks on, 2 weeks off - 20± Teredinidae.

In order to determine the effect of the chlorination on adult teredinidae two untreated wooden panels which had been submerged in the ocean for one month were selected, each panel showing from ten to twelve pairs of siphons extended and active. Both panels were exposed to continuous chlorination of 0.5 ppm. The siphons were immediately withdrawn and the entrance holes closed by the pallets. After exposure periods of fifteen and thirty minutes, respectively, to these conditions the panels were placed in flowing unchlorinated sea water. In both cases the pallets were withdrawn and the siphons extended. At the end of twenty-four hours the organisms were still alive and active, remaining so for a number of succeeding days.

Four additional panels which contained an average of ten active teredinidae were then exposed to intermittent chlorination of 3.0 ppm, 2 hours on and 2 hours off. After periods of exposure varying from 2 hours to 5-3/4 hours, all of the panels were removed to fresh sea water. Again all the mature organisms had survived and continued to carry on normal activities, even surviving shipment of the panels to the laboratory at Duxbury, Massachusetts, where they were placed in water 20°F. colder than that to which they were accustomed. After one week in the Duxbury water they were still active.

It is obvious that comparatively short exposures to the concentrations of chlorine mentioned had no immediate effect on the organisms and also did not disturb them to the extent that a delayed kill resulted.

During the summer of 1951 another series of tests were designed involving combinations of chlorination and elevated temperatures according to the following schedule:

#1 - Control - untreated sea water.

#2 - 0.25 ppm of chlorine, continuously.

#3 - No chlorine. Temperature of flowing water raised to 110°F, 30 mins. per week.

#4 - 0.25 ppm of chlorine continuously, plus raising temperature of water to 110°F. for 30 mins. per week.

#5 - 1.00 ppm of chlorine, 1 hour in 6.

#6 - 1.00 ppm of chlorine, 1 hour in 6, plus raising temperature of water to 110°F. for 30 mins. per week.

#7 - 1.00 ppm of chlorine, 1 hour in 12.

#8 - 1.00 ppm of chlorine, 1 hour in 12, plus raising temperature of water to 110°F. for 30 mins. per week.

In this case new wooden test blocks 2"x4"x4" were placed in the weir boxes as well as panels 6"x6"x1" which had been submerged in the ocean for some time until they contained active adult teredinidae. Operation of the apparatus began on July 27, 1951 and continued until December 7, 1951. The results of the examination of the exposed specimens were as follows:

#1 - Control - new block - Moderate *Limnoria* activity in springwood to a depth of 1/8" with all organisms active. Block well filled with *Bankia gouldi*.

6x6 panel - Panel completely destroyed by *Bankia* and disintergrating. Numerous live *Limnoria*.

#2 - 0.25 ppm chlorine continuously - New block - No attack.

6x6 panel - Panel in approximately same physical condition as when placed on test. *Bankia* all dead. *Limnoria* tunnels empty.

#3 - No chlorine. Temperature raised to 110°F. 30 mins. per week.

new block - 13 *Limnoria* tunnels, 1 live *Limnoria*. No *Bankia* present.

6x6 panel - Panel in approximately same physical condition as when placed on test. *Bankia* all dead. All *Limnoria* tunnels empty.

#4 - 0.25 ppm chlorine continuously, plus temperature raised to 110°F. 30 minutes per week.

new block - 4 empty *Limnoria* tunnels. No *Bankia*.

6x6 panel - Panel in approximately same physical condition as when placed on test. *Bankia* all dead. All *Limnoria* tunnels empty.

#5 - 1.0 ppm chlorine, 1 hour in 6.

new block - 70± *Bankia*, several of which were dead. 3 empty *Limnoria* tunnels.

6x6 panel - Destruction of wood proceeded to some extent beyond the original condition,

not, however, as far as in case of Control. All <u>Bankia</u> dead and <u>Limnoria</u> tunnels empty.

#6 - <u>1.00 ppm chlorine</u>, 1 hour in 6, plus temperature raised to 110°F. 30 minutes per week.

new block - 3 empty <u>Limnoria</u> tunnels. No <u>Bankia</u>.

6x6 panel - Panel in approximately same physical condition as when placed in test. <u>Bankia</u> all dead and <u>Limnoria</u> tunnels empty.

#7 - <u>1.00 ppm chlorine</u>. 1 hour in 12.

new block - Well filled with <u>Bankia</u> about half of which were alive. 75± empty <u>Limnoria</u> tunnels.

6x6 panel - Panel destroyed to nearly the same extent as the Control.

#8 - <u>1.00 ppm chlorine</u>. 1 hour in 12, plus temperature raised to 110°F. 30 minutes per week.

new block - No borers.

6x6 panel - Panel in approximately same physical condition as when placed in test.

Three additional 6"x6" panels previously exposed to marine borer activity were placed in the hot water apparatus from July 27th to December 7th according to the following schedules:

1.	Normal sea water.	Panel well disintergrated.
2.	Temperature of water raised to 100°F., 30 minutes per week.	Destruction of wood less than Control, but more than in original condition.
3.	Temperature of water raised to 120°F., 30 minutes per week.	Panel in approximately same condition as when placed on test.

The preceding data would certainly indicate that certain residuals of chlorine and ranges of temperature applied over comparatively short periods of time have a very definite effect on the activities of marine borers. Under the conditions of the tests it would seem that:

1. Lower residuals of chlorine, applied continuously, are much more effective for control than much larger amounts applied intermittently, although the latter show some degree of graduated effectiveness.

2. When exposed for short periods up to 5 hours, mature Bankia gouldi are able to survive the action of as much as 3.00 ppm of chlorine with no apparent ill effects, but when exposed for longer periods the organisms are killed.

3. Small residuals, when applied continuously, tend to prevent the original infestation by the organisms.

4. The elevation of water temperature to 110°F. for as little as 30 minutes per week consistently prevented the infestation of test blocks by Bankia gouldi, and halted the activity of mature organisms. Raising the temperature to 100°F. for the same length of time, while apparently having some effectiveness when compared with normal temperatures, was not as satisfactory as temperatures of 110°F. and 120°F.

5. Limnoria lignorum seems to be somewhat less affected by the elevated temperatures than is Bankia gouldi.

(Contribution from the Basic Sciences Research Department, U. S. Naval Civil Engineering Research and Evaluation Laboratory, Port Hueneme, Calif.)

TOXIC EXTRACTIVES OF GREENHEART

by Peter J. Hearst, Richard W. Drisko, Thorndyke Roe, Jr., and Herbert McKennis, Jr.

The commercial wood, greenheart, variously identified as Demerara Greenheart, Nectandra Rodioei, or Ocotea Rodioei, has long been recommended as a timber of choice for the construction of waterfront structures where marine borer activity is high.[1] The natural resistance of greenheart wood, now employed in many piers under the cognizance of the Bureau of Yards and Docks, has been occasionally attributed to the hardness of the material. This remains a possibility.

Van Iterson[2], in considering the resistance of certain woods, states that greenheart, with a silica content of less than half of one per cent, does not contain sufficient silica to endow it with any great resistance. Manbarklak on the contrary, which contains one and one half per cent silica is presumed to owe its resistance to silicious inclusions. Van Iterson believed the resistance of greenheart to be due to the presence of very poisonous alkaloids.

Baldwin[3] states that greenheart owes its power of resistance to its texture, to the presence of the alkaloid known as bebeerine, and to the resinous tyloses. Many others have attributed the resistance of greenheart to the presence of the alcohol-soluble alkaloid, bebeerine.

The oft-asserted protective action of bebeerine apparently finds its only support in the early work of Barger and Harrington[4]. These investigators impregnated blocks of Baltic fir with an alcoholic extract of greenheart sawdust and found that these blocks resisted Teredo attack for two seasons. From the alcoholic extract Barger and Harrington[5] obtained one-tenth of one per cent, presumably based on the weight of the sawdust, of a non-crystalline material reportedly corresponding to bebeerine. No evidence, however, is presented to verify the identity of their material with bebeerine.

It thus appeared well worth while to investigate greenheart more thoroughly from a chemical point of view and to determine what kind of toxic substances might be present in the wood. It was desired particularly to isolate and study the alkaloids which it contains, and to test these alkaloids to find out which ones, if any, were toxic to marine borers. If bebeerine, or some other alkaloid, is the active principle in greenheart, variation in the alkaloid content of different samples of the wood might possibly be the reason for the long life of greenheart pilings in some instances and the relatively short life in others.

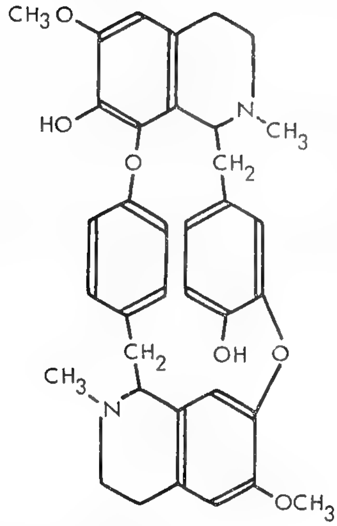
Of course, there still remains the possibility that the protective principle is not an alkaloid at all, but some other alcohol-soluble material. This material might possibly turn out to be simple enough to be manufactured readily. If the protective principle is more complicated, it would be worth while to synthesize and test similar compounds, some of which might become economically feasible materials for wood impregnation.

Alkaloids are sometimes defined as nitrogen-containing basic compounds which occur in plants and more rarely in animals. They usually have physiological activity. Figure 1 shows two alkaloids. One of them is bebeerine in which we are particularly interested. The other is a very abundant alkaloid with a confusingly similar name, berberine. Both happen to be members of the isoquinoline group. Bebeerine is also a member of the bis-benzyl isoquinoline sub-group. It is a 36 carbon molecule with two basic nitrogen atoms and two free phenolic groups. It can therefore be considered as a phenolic amine, a type of compound which will be further discussed by Mr. Roe in the paper which follows.

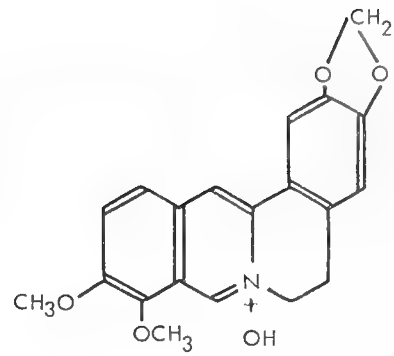
A surgeon in the British Royal Navy, a Dr. Rodie, in 1834 found that greenheart bark contained an alkaloid which was useful against undulant fever. In 1840, Maclagan[6] began an investigation of the bark of the greenheart or bebeeru tree and obtained from it an ether-soluble alkaloid and an insoluble alkaloidal residue. The former he named bebeerine and the latter sipeerine after the native and the Dutch names for the greenheart tree. In 1869, Maclagan and Gamgee[7] published preliminary results of an investigation of the bases in greenheart wood. They isolated a chloroform-soluble alkaloid, nectandria, and a chloroform-insoluble base, and showed the presence of still another base. Except for possible duplication, greenheart thus contained at least five alkaloids. The authors apparently published no further results.

In 1838, Wiggers[8] isolated the alkaloid pelosine from Cissampelos pareira and also from the raw medicine obtained from Radix pareirae bravae. The name pareira brava is derived from the Portuguese for wild grapevine and the root of this plant was first imported into Germany from South America in 1688. In 1869, Flückiger[9] showed that pelosine and bebeerine were identical. The latter name took precedence, but subsequent work on bebeerine was carried out with material derived from pareira brava and not with that obtained from greenheart. In fact, no further chemical studies of the wood or bark of the greenheart tree appear to have been published, except for the above mentioned brief work of Barger and Harrington.

Recently there has been much interest in curare alkaloids which are obtained from the same species of plants as pareira brava. Curare active compounds induce flaccidity of striated muscle and have become increasingly useful in abdominal surgery and other applications where muscle relaxation is important. The chemical frequently used for this purpose is the quarternary alkaloid, tubocurarine chloride. It was originally obtained from tubo curare, one of three types of curare used as arrow poisons by the South American Indians. It occurs together with a closely related tertiary



BEBEERINE



BERBERINE

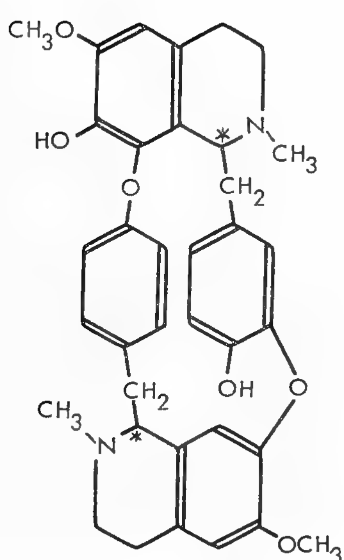
Fig. 1

ALKALOIDS ISOLATED FROM GREENHEART BY MACLAGAN IN 1840-1869

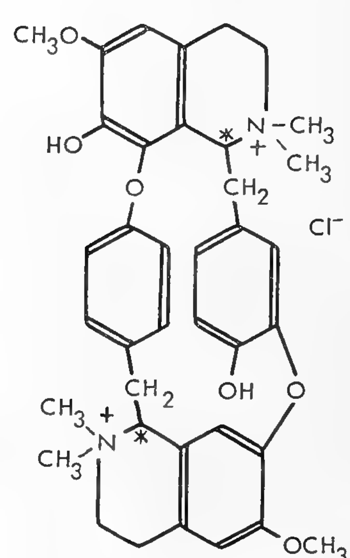
BARK
1. An ether soluble alkaloid - Bebeerine
2. An ether insoluble alkaloid - Sipeerine

WOOD
1. A chloroform soluble alkaloid - Nectandria
2. A chloroform insoluble alkaloid
3. A third base was present

Fig. 2



l - CURINE



d - TUBOCURARINE

Fig. 3

alkaloid, curine. The latter was shown by Spath[10] to be identical with bebeerine. Spath[11] later suggested the correct formula, for which King[12] gave experimental evidence in 1939. This involved a two-stage Hofmann degradation of dimethyl bebeerine to the methyl bebeerilene, subsequent oxidation to the two acidic fractions shown, and finally the synthesis of both of these molecules for comparison.

The most direct way of attacking our problem would be to purchase some bebeerine and to test its activity against marine borers. Unfortunately, the matter was not quite so simple, as there were no suppliers.

The best source for bebeerine still appeared to be pareira brava. However, the bebeerine content of this material varies from about 30% of the crude alkaloids to little or no bebeerine[10], and the bebeerine obtained can be the levorotatory, the dextrorotatory, or the racemic form.[13]

Some pareira brava was obtained and the alkaloids were extracted esentially according to the procedure employed by King[14], which is shown in Figure 5.

According to previous workers,[10, 13, 14] the ether-soluble alkaloids are dissolved in methyl alcohol, and, on standing, crystals of bebeerine separate. However, the pareira brava which we extracted contained little or no bebeerine. The crude alkaloids were separated into a large number of fractions, none of which, according to their properties, contained bebeerine.

Similar results were obtained with a second shipment of pareira brava from a different supplier.

After much letter writing a firm in Scotland was located which had available a one pound quantity of commercial "Bebeerine Hydrochloride." From this black material we obtained the free bases which were conspicuously similar to those which we isolated from pareira brava. In fact, it turned out that the "Bebeerine Hydrochloride" did consist of the hydrochlorides of the total alkaloids from the root of pareira brava.

The crude bases from the "Bebeerine Hydrochloride" were extracted successively with benzene, methylene chloride, and methyl alcohol. The total solids from the benzene extract were dissolved in methyl alcohol. When the solution was cooled, a white precipitate (12% based on the crude alkaloids) melting at 285° was obtained. The material remaining in solution was separated by the process of "fractional crystallization" into eight amorphous fractions, which according to their properties consisted of four or more compounds. The methyl alcohol extract was similarly separated into six fractions consisting again of four or more compounds.

The material melting at 285° was recrystallized from methyl alcohol and chromatographed on alumina to give crystalline isochondrodendrine, melting at 302°. The material had the expected physical and chemical properties and its identity was confirmed by the preparation of the dimethiodide.[15]

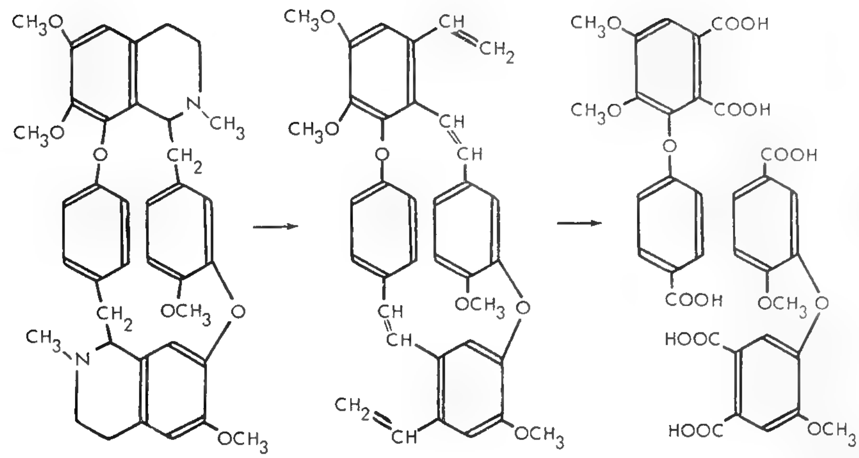


Fig. 4

DEGRADATION OF DIMETHYLBEBEERINE

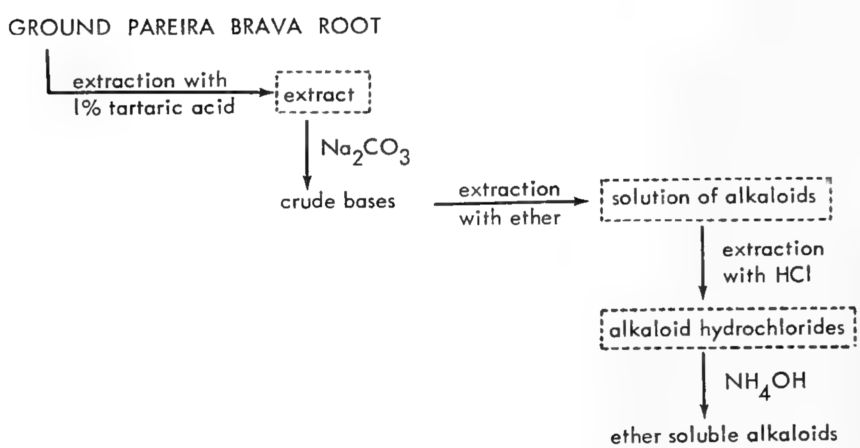


Fig. 5

EXTRACTION OF THE CRUDE BASES FROM "BEBEERINE HYDROCHLORIDE"

SOLVENT	YIELD	COLOR	
benzene	31%	light amber	methyl alcohol → 12% precipitate, white, m.p. 285°; 19% in solution → 8 fractions consisting of 4 or more compounds
methylene chloride	23%	dark amber	
methyl alcohol	32%	brown	→ 6 fractions consisting of 4 or more compounds
residue	11%	dark brown	

Fig. 6

The isochondrodendrine content of the commercial "Bebeerine Hydrochloride" was approximately twenty per cent of the total, but no bebeerine could be isolated.

Isochondrodendrine is a structural isomer of bebeerine. It has the same number of atoms and the same functional groups and differs only in the position of one of the ether linkages. Due to this similarity, it is being further investigated for activity against marine borers.

We next turned our attention to greenheart itself. Generous samples of bark and sawdust were received from the Willems Timber and Trading Company and the Greenheart and Wallaba Timber Company. To both of these companies we are greatly indebted. The nitrogen contents of dried greenheart samples show small differences which are not significant for Dumas determinations.

Samples of greenheart bark from both companies were percolated in an apparatus which had a capacity of nine pounds of ground bark. The extractions were carried out as in the case of the pareira brava. The ether-soluble alkaloids from the two samples were cream colored powders having specific rotations ($[\alpha]_D$, c=1.00 in methyl alcohol) of +125° and +129° respectively. Bebeerine is reported to have a specific rotation of +300°.

Work on the separation of the crude alkaloids into pure components so far has been of a preliminary nature. The alkaloids are quite unstable and discolor slowly on exposure to light. A sample in methyl alcohol solution which was kept in a refrigerator changed its specific rotation from +125° to +78° in six months.

A sample having a specific rotation of +121° was subjected to chromatographic analysis. The results are shown in Figure 9. The solvents used were progressively more concentrated solutions of methyl alcohol in methylene chloride. There may be at least as many substances as solvent pairs employed. Even in this chromatography some change apparently took place since the specific rotations of the fractions are considerably less than expected.

The chemical and physical properties of the fractions isolated in our preliminary study do not correspond with those reported for the alkaloid bebeerine. Until further evidence is obtained any mechanism which attempts to explain the resistance of greenheart to marine borers on the basis of the toxic action of bebeerine must be regarded as somewhat doubtful. The possibility remains that some other alkaloid or some other substance is responsible.

An alcoholic extract of greenheart sawdust was prepared essentially according to the method of Barger and Harrington.[5] This extract contains a large percentage of non-basic material and only a very small amount of alkaloids. Pine blocks, impregnated with the total extract have been submitted to the Marine Laboratory, University of Miami, for investigation of marine borer resistance. Similar test pieces impregnated with the crude

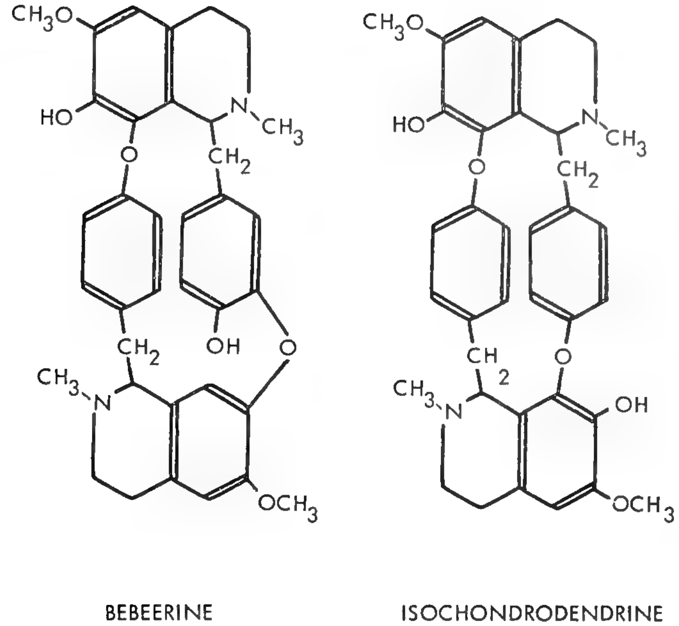


Fig. 7

NITROGEN CONTENT OF DRIED GREENHEART SAMPLES

Fig. 8

SUPPLIER	BARK	SAWDUST
Willems Timber and Trading Co.	0.83% N	0.54% N
Greenheart and Wallaba Timber Co.	0.58% N	0.41% N

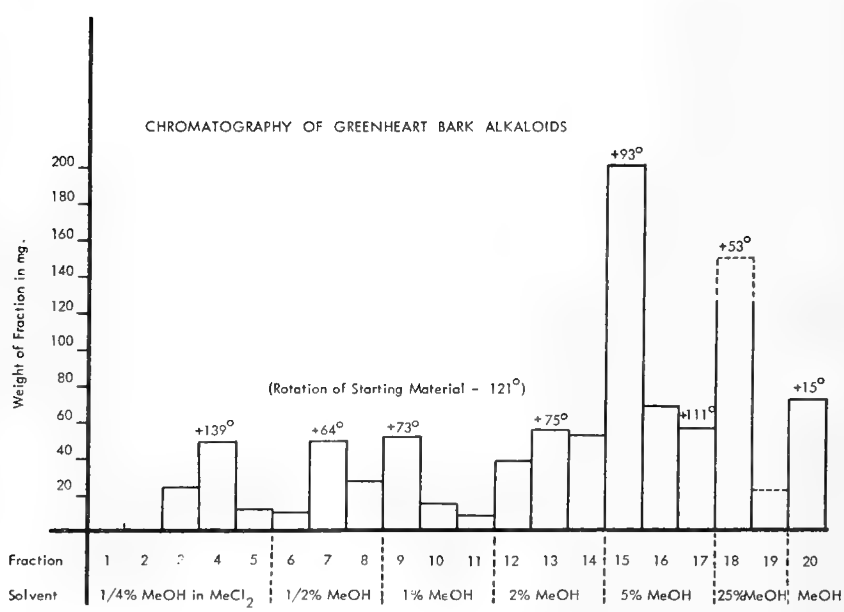


Fig. 9

ether-soluble alkaloids from greenheart bark and with isochondrodendrine also have been submitted. We wish to thank Dr. F. G. Walton Smith and his colleagues at the Marine Laboratory for their kind collaboration.

We also wish to acknowledge the many excellent microanalyses carried out by Mr. Robert J. Brotherton of our laboratory.

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(Contribution from the Basic Sciences Research Department, U. S. Naval Civil Engineering Research and Evaluation Laboratory)

STUDIES ON SYNTHETIC PHENOLS AND ARYLAMINES FOR MARINE BORER INHIBITION

By Thorndyke Roe, Jr., Robert L. Alumbaugh, and Herbert McKennis, Jr.

One approach to the problem of deterioration of wooden structures by marine borers lies in economical synthetic pesticides which can effectively preserve woods over a long period of time. Synthetic organic chemicals have received wide usage in the preservation of timbers where utilization is restricted to non-marine conditions. Many of these compounds belong to the general class of aromatic alcohols called phenols. In Figure I, four common nitrophenols which have enjoyed some popularity as preservatives are shown. Introduction of the nitro group enhances fungicidal activity, but probably contributes to the corrosive action of the phenols on fastenings (1).

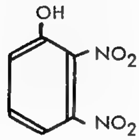
Chlorinated phenols (Fig. I), especially the familiar pentachlorophenol, have found wide application. Pentachlorophenol, while effective in many environments, is not recommended for conditions where wood will be immersed in salt water (2).

It is interesting that Clapp and Richards reported that creosote which was low in phenols (cresylic acids) had lost some of its effectiveness as a marine borer deterrent (3). Phenols as a group are noted for the wide biological spectra of their toxic activity. The series of phenols currently under study in this laboratory are all derived from benzylamine and are illustrated in Fig. IV.

Presence of the amino group may serve to inhibit corrosive action. This point, however, has not been investigated. The series is of further interest since many of the intermediates in the chosen synthetic routes have been shown to possess or are related to compounds with marked local anesthetic activity.

Local anesthesia, according to the theory of Thimann, results from interference with the production or utilization of acetylcholine (4). The experimental work of Bullock establishes a close relationship between inhibition of cholinesterase and production of local anesthesia. (5). Many economic poisons may, in part at least, owe their effectiveness to interference with acetylcholine metabolism which is attributable to their inhibition of cholinesterase (6).

Figure V shows the preparation of three para-substituted benzyl morpholines. The para nitro and the para amino compounds are both known to possess local anesthetic activity (7).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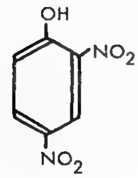
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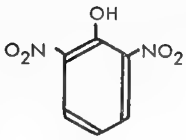
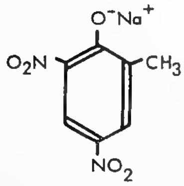
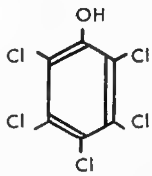
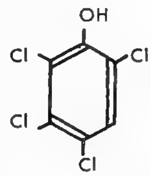

2,6-dinitrophenol


sodium dinitro-o-cresolate


pentachlorophenol


2,4,5,6-tetrachlorophenol

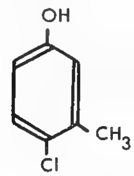
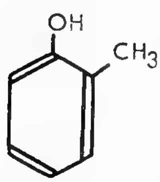
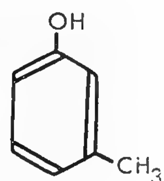
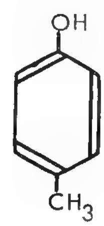
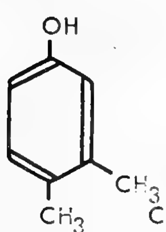

parachlorometacresol

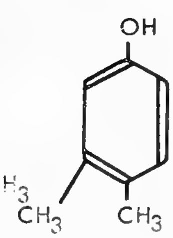
Fig. I. Nitro and Chloro Phenols Used in Wood Preservation

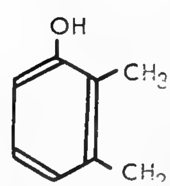

o-cresol

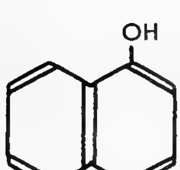

m-cresol

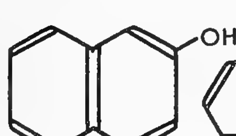

p-cresol

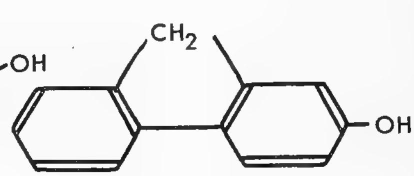

1,3,4-xylenol

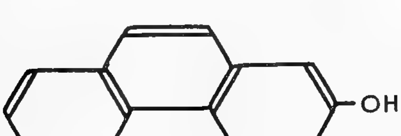

1,4,5-xylenol

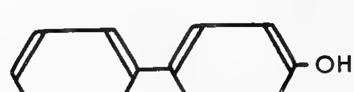

1,2,3-xylenol


α -naphthol


β -naphthol


2-hydroxyfluorene


2-phenanthrol


4-hydroxydiphenyl

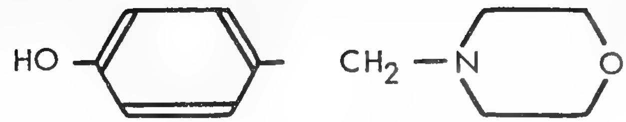
Figs. II & III. Some Common Phenols in Creosote

A methanol solution of commercially available p-nitrobenzyl chloride is refluxed with an excess of morpholine to yield N-p-nitrobenzyl morpholine. Leffler and Volwiler produced this compound from the same two reactants in benzene solution (7). The nitrocompound is reduced with hydrogen in the presence of Adams' catalyst at three atmospheres yielding N-p-aminobenzyl morpholine. This method was found to be better than the iron-alcohol reduction employed by Leffler and Volwiler (7). Our yields were 98% as opposed to a 76% yield obtained by the chemical method of the former workers. The amino compound is converted to the intermediate diazonium salt by reaction with sodium nitrite and sulfuric acid. Decomposition of this salt with a boiling 70% sulfuric acid solution gives a 38% yield of N-p-hydroxybenzyl morpholine.

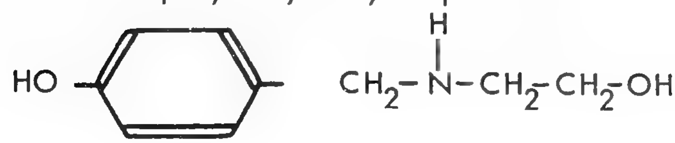
The preparation of N-p-hydroxybenzylaminoethanol is illustrated in Fig. VI. p-Hydroxybenzaldehyde is added to an ethanol solution of ethanolamine. The Schiff base, II, separates out almost immediately in 77% yield. The latter is readily reduced with hydrogen in the presence of Adams' catalyst at three atmospheres to give a 95% yield of N-p-hydroxybenzylaminoethanol, isolated as an oil. For analysis, the compound is converted to the 5-nitrobarbituric acid derivative salt.

For comparison purposes with the benzyl morpholine compounds previously described, the nitro and amino analogues of N-p-hydroxybenzylaminoethanol were prepared as shown in Fig. VII. A methanol solution of p-nitrobenzyl chloride is refluxed with excess ethanolamine to give N-p-nitrobenzyl-aminoethanol in 58% yield. Barbiere reported the synthesis of this compound by mixing the two reactants directly, but the reaction is very exothermic and considerable decomposition may occur (8). Reduction of the nitro compound with hydrogen in the presence of Adams' catalyst at three atmospheres yields N-p-aminobenzylaminoethanol in 83% of the theoretical amount.

The preparation of the diethanol compounds is shown in Fig. VIII. Barbiere synthesized 2,2'-(p-nitrobenzylimino) diethanol by mixing p-nitrobenzyl chloride and diethanolamine (8). However, the reaction, like that for the making of the monoethanol compound by this method, is very exothermic and considerable decomposition may occur. Again, our method consists of refluxing a methanol solution of p-nitrobenzyl chloride with an excess of diethanolamine to give 2,2'-(p-nitrobenzylimino) diethanol in 62% yield. Reduction of the nitro compound with hydrogen in the presence of Adams' catalyst at three atmospheres gives a quantitative yield of 2,2'-(p-aminobenzylimino)diethanol, isolated as an oil. For analysis, the compound is converted to the 5-nitrobarbituric acid salt derivative. Conversion of the amino compound to the corresponding phenol has not yet been accomplished. In view of the known susceptibility of tertiary amines to nitrous acid under some conditions, the method used in going from 2,2'-(p-aminobenzylimino) diethanol to the phenol may have to be modified.

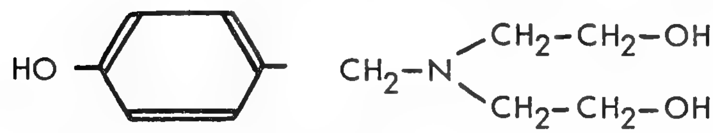


N-p-hydroxybenzylmorpholine

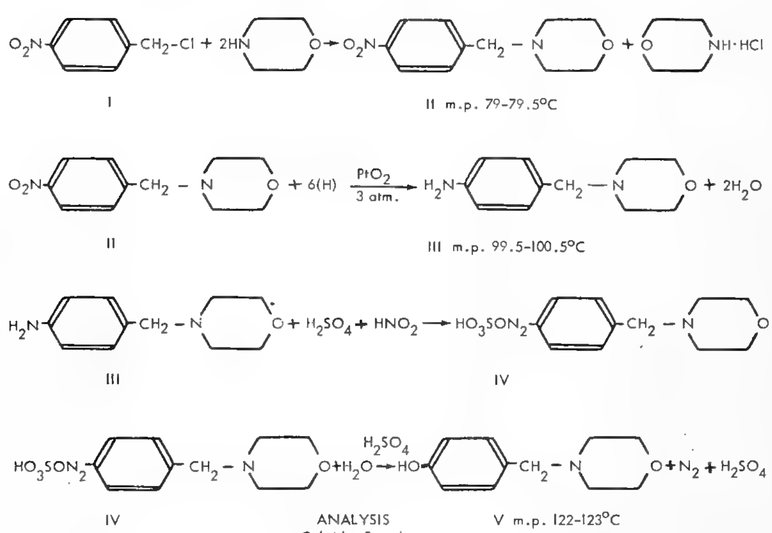


N-p-hydroxybenzylaminoethanol

Fig. IV



2,2'-(p-hydroxybenzylimino) diethanol



ANALYSIS

		Calc'd	Found
II	%N	12.6	12.4
V	%C	68.4	68.54
	%H	7.8	7.60
	%N	7.25	7.41

Fig. V

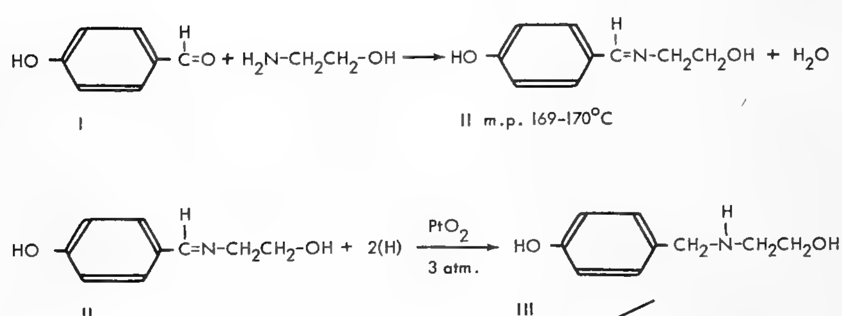
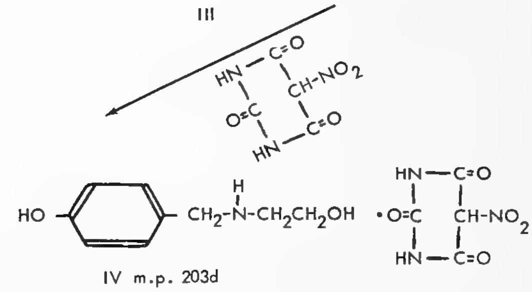


Fig. VI



ANALYSIS

		Calc'd	Found
II	%N	8.49	8.19
IV	%N	16.6	16.5

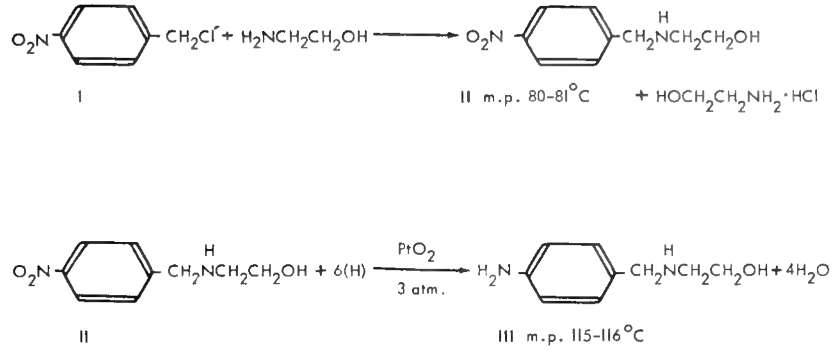


Fig. VII

ANALYSIS

		Calc'd	Found
III	%C	65.03	65.00
	%H	8.49	8.11
	%N	16.85	16.60

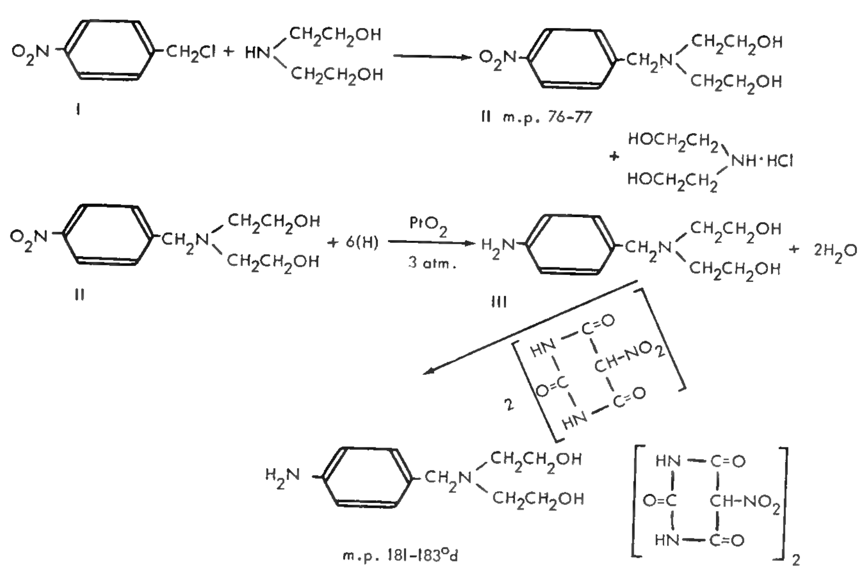


Fig. VIII

At the present time, some of the compounds which we have described are under investigation at Port Hueneme. Dr. Walton Smith of the Marine Laboratory, University of Miami, has generously offered to study the action on blocks treated with some of these materials in the accelerated testing procedure which has been developed in his laboratory. We are especially grateful to Dr. Smith and his colleagues for this work and to Mr. Robert J. Brotherton of the Basic Sciences Research Department, U. S. Naval Civil Engineering Research and Evaluation Laboratory for the microanalyses on the new compounds which were synthesized.

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(Contribution from the Marine Laboratory, University of Miami)

VARIATION OF GLYCOGEN AND NITROGEN CONTENT OF SHIPWORMS WITH GROWTH AND SEASON*

by Leonard J. Greenfield

Monthly analyses of the glycogen and nitrogen content of shipworms were accomplished between July 1951 and May 1952. The above components were selected as indices of stored protein and carbohydrate in the organisms. The average glycogen content of the shipworms over 25 mg. dry weight was found to be slightly above 30%. From 0 to 25 mg. dry weight, a steady increase in the percent concentration of this component was apparent. Increasing nitrogen content was observed in the smallest of the specimens until a maximum value of 2.17% occurred in the 10-14.9 mg. weight group. Sexual maturity of Teredo pedicellata was achieved in this weight group under the conditions observed.

No seasonal change in the nitrogen and glycogen content was noted, and there was no apparent difference in the concentration of these components between gravid and non-gravid individuals of the same size range.

A greater concentration of glycogen in the prenatal larvae than in the free-swimming larvae was recorded, and it was evident that a continued free-living existence would deplete the supply of this material to a minimum. This is based on the fact that liberated larvae do not feed and are dependent on the glycogen reserves passively obtained from the parent shipworm. Once attachment has taken place and feeding commences, the reserve supply of carbohydrate needed for the resumption of metabolic activity is replenished.

The importance of wood used as a source of food in the diet of the organism was also studied. In addition to wood polysaccharide utilization, indications are that wood contains sufficient nitrogen to account for that found in Teredo pedicellata. Utilization of plankton as a source of nitrogen was also apparent. This was demonstrated by growing the shipworm in cellulose panels containing no nitrogen.

*Abstract of article from Bull. Mar. Sci. of the Gulf and Caribbean, Vol.2, No. 3, pp. 486-496, March, 1953.

(Contribution from the Marine Laboratory, University of Miami)

THE ORIGIN AND DISTRIBUTION OF NITROGEN IN *TEREDO**

by Reuben Lasker

Abstract

The amino acid content of acid-hydrolyzed *Teredo bartschi* Clapp of all ages has been compared chromatographically with hydrolysates of pine wood and of nannoplankton. Wood appears to be deficient in the aromatic amino acids phenylalanine and tyrosine, in the heterocyclic amino acid proline, and in valine, all of which are found in *Teredo*. Hydrolysates of nannoplankton contain all of these missing amino acids except phenylalanine. It is suggested that both wood and suspended nannoplankton are used as dietary sources of nitrogen by *Teredo*.

*This paper has been presented to the Editors of the Biological Bulletin for publication.

(Contribution from the Research Department, Battelle Memorial Institute)

RESEARCH ON HYDROCARBON OILS

by Ray E. Heiks

ABSTRACT*

In order to investigate thoroughly hydrocarbon oils as wood preservatives, a wide variety of samples of creosote oils and petroleum oils were collected. The creosote oils included distillates from coke oven, vertical retort, and horizontal retort tars. The petroleum samples included fuel oils, recycled gas oils, and other oils described as "highly aromatic."

The initial experimental work involved studies of the infrared spectra of all of the oils in efforts to determine whether the creosote oils differed fundamentally from the petroleum oils. The results of these studies revealed that the creosote oils contained a greater predominance of aromatic carbon-hydrogen bonds than the petroleum oils. The ratio of the optical density of aliphatic and/or naphthenic carbon-hydrogen bonds to aromatic carbon-hydrogen bonds varied from 11 to 36 for the petroleum oils and between 0.5 to 6.0 for the creosote oils. Comparison of the infrared spectra of all creosote oils indicates that they are quite similar and significantly different from the petroleum oils. Many absorption bands found in creosote oil are missing in the petroleum oils, whereas, all of the bands found in petroleum are also found in creosote oil.

In an effort to study the oils more precisely, two samples of creosote were subjected to fractionation under vacuum, in a column 39 inches long by 3/4 inches in diameter, packed with 1/8 by 1/8-inch stainless steel gauze. The column had an efficiency of 50 plates at atmospheric pressure. A 1500-ml. charge was cut into 1 percent volume fractions. The reflux fraction was 20 to 1. A total of 87 cuts were taken from the coke oven creosote and 70 cuts were taken from a vertical retort creosote. Fractional distillation under vacuum was considered to be a good means of separating creosote into fractions containing a small number of individual components. It was found that very poor separations were obtained, probably because of the large number of azotropes that are formed in the mixture. An illustration of the poor separation obtained is shown by the fact that phenol was found in fractions boiling over a 43-degree temperature range and naphthalene in fractions boiling over a 53-degree temperature range. A mixture of phenol and naphthalene was found in Fractions 2 through 6, boiling between 183 and 211°C. It was concluded that distillation alone did not appear to be adequate in separating creosote into its components.

In comparing a vertical retort creosote with a coke oven creosote, infrared spectra showed that phenolic OH compounds appeared in all fractions boiling up to 380°C., and there was even a trace in the last fraction boiling at 395°C., whereas in the case of the coke oven creosote, no significant amount of phenolic OH compounds were found in any fractions

boiling above 203°C. Pyrene and phenanthrene were positively identified in both samples. This work is continuing.

In an effort to further determine whether fundamental differences exist between petroleum oils and creosote oils, dielectric-constant measurements on three samples of petroleum gave values ranging from 2.44 to 2.69, whereas creosote oils gave values of 4.56 to 7.94. Further, velocity of sound measurements on two petroleum oils were in the range of 1476 and 1507 meters per second, whereas two creosote oils gave values of 1530 and 1590 meters per second.

Solvent extraction studies using β,β'-oxydipropionitrile indicate that this solvent is very unique in its ability to separate aromatic compounds with a small amount of alkyl substitution from those containing a larger amount. It is also very sensitive to the presence of naphthenic groups in an aromatic compound. It is potentially valuable as a means of detecting the presence of petroleum products in creosote oils.

*A portion of this work is reported in the Proceedings of the American Wood-Preservers' Association, volume 48, pages 53 to 83, 1952. Additional portions will appear in the Proceedings of the American Wood-Preservers' Association, volume 49, 1953.

(Contribution from the Naval Research Laboratory)

INVESTIGATION OF THE PHENOLIC FRACTION OF CREOSOTE*

by T. R. Sweeney and C. R. Walter, Jr.

Abstract

A study of the tar-acid fraction of A.W.P.A. Grade 1 creosote has been made by selective extraction of the latter with aqueous and Claisen alkali. This study indicated the presence of three groups of hydroxylic compounds: one extractable with aqueous alkali, one extractable only with Claisen alkali, and one unextractable with either aqueous or Claisen alkali. Spectrophotometric measurements indicated the presence of unhindered alkylated phenols in the aqueous alkali-soluble fraction and of unhindered phenols of higher molecular weight in the fraction extractable only with Claisen alkali. The presence of phenylphenols was indicated in both fractions. A material balance of the fractions showed that the quantity of phenols extractable with Claisen alkali was about twice that extractable with aqueous alkali. Of the total oxygen of the original creosote, somewhat more than half was extractable with Claisen alkali. A comparison of the oxygen content of the fractions as determined by difference with the oxygen content calculated from active hydrogen determinations indicated that the oxygen could largely be accounted for as hydroxyl.

*This paper appeared in full in NRL Report No. 3940, 10 pp. & figs., February 6, 1952.

(Contribution from the Yale School of Forestry)

TROPICAL AMERICAN WOODS FOR DURABLE WATERFRONT STRUCTURES[1]

by Frederick F. Wangaard

Unless given a preservative treatment, only a limited number of domestic woods are adapted to uses that involve conditions favorable to the development of wood-rotting fungi or to marine borer activity. Through effective methods of preservative treatment, the life of domestic woods under these conditions can be effectively increased. A number of tropical woods, however, have been employed without treatment for such purposes over prolonged periods and the question is raised as to the possibilities for making wider use of these and other naturally resistant species.

Under the sponsorship of the Office of Naval Research and the Bureau of Ships of the Department of the Navy, the Yale School of Forestry has been engaged since 1947 in a study of the properties and uses of woods from the American tropics. The scope of the over-all study includes determination of mechanical properties, density, shrinkage, decay resistance, rate of moisture absorption, resistance to weathering, and the characteristics of the wood in relation to seasoning, paint holding, machining, gluing, and steam bending. Through arrangement with the William F. Clapp Laboratories at Duxbury, Massachusetts, certain of these woods are being subjected to exposure in infested waters to determine their resistance to marine borer attack. Other tests are conducted on selected woods at the New York Naval Shipyard to determine resistance to fire and abrasion and at the Institute of Paper Chemistry, Appleton, Wisconsin, to determine the chemical composition of certain of these woods.

The successful use of wood for durable water front structures involves, first of all, the selection of species combining the requisite mechanical properties to sustain applied loads with resistance to deterioration. Decay is the principal agency of deterioration above the water line, whereas sub-surface structural members are subjected to attack by marine borers in infested waters. Other forms of deterioration to which certain parts of water front structures are exposed include weathering and mechanical wear. In addition to the qualities of strength and resistance to deterioration a wood showing low shrinkage would generally be preferred to another characterized by high shrinkage values, not only from the standpoint of dimensional stability of the structure, but also from the lesser warp that would ordinarily accompany lower shrinkage.

[1] The data presented in this paper were gathered as a part of a general study of the properties of tropical woods being conducted in cooperation with the Office of Naval Research and Bureau of Ships, U. S. Navy Department, under Contract N6ori-44, Task Order XV, Project No. NR-330-001.

The woods shown in Table 1 have been selected from a large number of species for which mechanical testing in both the green and air-dry conditions has been completed. In addition to the more important mechanical properties, the table shows weight per cubic foot, radial and tangential shrinkage, resistance to checking and splitting upon weathering, decay resistance, and marine borer resistance. Relatively few of the species listed, however, have been subjected to marine borer testing.

Species Suitable for Durable Above-Water Construction

The most suitable of these woods from the standpoint of durable above-water construction are grouped in three classes-- Greenheart--White Oak--Southern Pine--Douglas Fir--on the basis of approximate strength properties and are discussed individually in this section. Most of these woods are considered in greater detail in other reports on this project (3, 5, and 8). *Timbers of the New World* (6) has been drawn on freely as a source of information relative to the distribution and character of the timber.

Very strong woods (Greenheart class)

1. Almendro (*Coumarouna oleifera*), Cumarú (*Coumarouna odorata*). These closely related species are combined here for discussion. Almendro is common to very plentiful in the lowland forests on the Atlantic side of Central America from Nicaragua to Panama. The tree is commonly large, sometimes reaching a diameter of 6 feet and a height of 180 feet. The bole of mature trees is virtually cylindrical and clear for 50-70 feet above the heavy buttresses to the first massive limbs. Because of their large size and the hardness of the wood, Almendro trees are frequently left standing in areas temporarily cleared for agriculture.

Cumarú, the usual name for Tonka Bean in Brazil, is common in many forest areas in Venezuela, the Guianas, and the Amazon region of Brazil. The trees are frequently $1\frac{1}{2}$ - $2\frac{1}{2}$ feet in diameter and 80-120 feet in height. The cylindrical bole is generally clear to heights of 60-80 feet.

The wood of these species is similar to that of Greenheart in density and strength. Shrinkage is low relative to its density and resistance to checking and splitting is high. Timbers of this genus have a reputation for outstanding durability with respect to decay. Cumarú has proved to be one of the best crosstie woods in Brazil not only because of its durability but also because of its freedom from splitting. Both woods are used for heavy construction especially where durability is a factor. Because of their somewhat oily nature and the ability of the wood to acquire a smooth, polished surface under conditions of heavy wear, Almendro and Cumarú have been tested as Lignum Vitae substitutes.

2. Bulletwood (*Manilkara bidentata*). This species is common in northern South America, Panama, and parts of the West Indies. Other species of Manilkara and closely related genera also occur throughout this range and extend through Central America. These related species are sometimes confused with *Manilkara bidentata*. The Bulletwood tree is typically large,

well-formed, and tall. It commonly attains diameters of 3-4 feet and heights of 100-150 feet. Buttresses are usually small or lacking.

The wood is generally comparable to Greenheart in density and in mechanical properties. Shrinkage values slightly exceed those of White Oak and the wood is rather prone to check upon weathering. Heartwood of Bulletwood has long been recognized for its high resistance to decay and insect attack. The National Park Service in Puerto Rico has reported that timbers of Ausubo (Manilkara bidentata), still sound after more than 400 years of service in buildings, have been re-used upon the reconstruction of historical sites. The wood lacks resistance to marine borers.

Bulletwood has a number of desirable characteristics that have resulted in a wide variety of local uses including flooring, foundations, bridge members, posts, poles, and railway ties. Its great strength, high wear resistance, and durability recommend it for heavy and durable construction.

3. Guayacán (Tabebuia guayacan, T. heterotricha). More than twenty species of Tabebuia have dark greenish-brown heartwood of high density, strength, and durability. These species range from southern Mexico through Central America and South America as far south as Argentina. Tabebuia guayacan and T. heterotricha are here referred to specifically. The former occurs in Central America, southern Mexico, and Colombia; the latter from Nicaragua to Venezuela. Guayacán trees are usually tall and straight, commonly 2-3 feet in diameter and 90-100 feet in height. The bole is cylindrical and free of branches for 40-50 feet. Heavy buttresses are usually limited to the basal 3 feet.

Except for the lower stiffness of Guayacan, this wood compares closely with Greenheart in its mechanical properties. Density is slightly less than that of Greenheart. In shrinkage, Guayacán is similar to White Oak. The wood is rated only fair in its resistance to the development of checks upon weathering. Guayacán heartwood is extremely durable with respect to decay and resistant to insect attack. It has been reported sound after 300 years' exposure in Panama.

Because of its durability and strength, Guayacán finds local use in house construction, railway crossties, heavy construction timbers, mine timbers, and marine construction.

4. Muira-juba (Apuleia molaris). This species is one of the larger trees of the Amazon valley forest of Brazil, sometimes exceeding 160 feet in height with a large bole. A related species, Apuleia leiocarpa, having a similar wood, is well known in Brazil and Argentina. Muira-juba attains its best development and is most commonly found on rich, moist but well-drained, clay soils.

The wood is considerably lighter than Greenheart and correspondingly weaker although its strength properties exceed those of most well-known domestic woods. Air-dry bending and crushing strengths and stiffness of Muira-juba, for example, are about 40 per cent higher than corresponding values for

White Oak. Shrinkage is low and resistance to weathering is excellent. Durability tests indicate high resistance to attack by wood-rotting fungi.

The properties of Muira-juba recommend its use in heavy durable construction, flooring, and general construction, particularly where exposure to weathering is involved.

5. Acapú (Vouacapoua americana). The range of this species includes parts of Surinam and French Guiana, but it attains its best development in the state of Pará, Brazil. The tree is tall but the unbuttressed bole only occasionally attains diameters greater than 2 feet. The species reputedly produces the best timber of French Guiana but is of infrequent occurrence there. In Brazil much of the readily accessible timber has been cut although considerable supplies are still available.

The wood is appreciably lower in density than Greenheart but, on the basis of available green strength values, only slightly lower than Greenheart in bending strength and stiffness and generally comparable in compressive strengths. Shrinkage is low in proportion to the density of the wood. Heartwood is highly resistant to decay and insect attack, and has demonstrated a high degree of resistance to marine borer attack at Harbor Island, North Carolina, although conflicting results have been reported from tests in Hawaiian waters (4).

The dark colored timber of Acapú is highly esteemed in Brazil for all kinds of heavy durable construction, flooring, and marine structures.

Strong woods (White Oak class)

1. Mylady (Aspidosperma cruentum). This species is found from southern Mexico through Central America to Colombia. The Mylady tree is moderate in size. In British Honduras few trees are larger than 1½ feet in diameter, although attaining heights in excess of 100 feet. In other parts of Central America diameters of 2-3 feet are recorded. The clear bole commonly extends for more than two-thirds the total height of the tree.

The wood is much stiffer than White Oak and is substantially stronger in most respects. Its shrinkage compares closely with that of Oak. Resistance to checking is fair. The wood is rated extremely durable with respect to decay and adapts the timber for use in heavy durable construction, railway crossties, sills, and framing.

2. Mora Amarilla (Chlorophora tinctoria). The tree and wood of Mora Amarilla are well known throughout tropical America. The species is widely distributed from southern Mexico to southern Brazil, Paraguay, and Argentina. Under good growing conditions and particularly in the southern part of its range, Mora Amarilla grows straight and tall, frequently to 2 feet in diameter and 60-80 feet in height with a clear bole of 20-35 feet. In some areas the trees attain diameters of 40 inches and heights of 90-120 feet. Although not abundant, the species is a constant factor in the forests of southern Brazil, Paraguay, and Misiones, Argentina.

The wood is superior to White Oak in all mechanical properties. It is characterized by moderate shrinkage and excellent weathering qualities. Heartwood of Mora Amarilla has long been recognized for its high degree of resistance to decay and insect attack. It is not resistant to marine borers, however.

Mora Amarilla is prized locally in the tropics for heavy durable construction. It is frequently used for piles, poles, foundation and bridge timbers, culverts, crossties.

3. Brazilian Louro (Aniba Duckei, A. cf. riparia, Ocotea sp.). In the Amazon region of Brazil there are a number of species known as Louro. The above-named species represent three of these. They are similar in appearance and almost identical in physical and mechanical properties. These three species are therefore grouped for the purpose of discussion. The Brazilian Louros, based on descriptions of the trees from which test material was obtained, attain diameters of about 2 feet and heights of 100 feet or more with a clear bole extending about two-third of total height. Little information is available concerning their abundance although, together with closely related species of the Lauraceae, they constitute a significant part of the forest.

The wood of the Brazilian Louros is comparable to White Oak in density, but is considerably stronger and stiffer than Oak. Only in compression across the grain, are they approximately equal to White Oak. Shrinkage is less than that of Oak, and resistance to checking and splitting upon exposure to weathering is very high. The timbers of the group are extremely resistant to decay.

Although their use has for the most part been limited to general construction, the excellent properties of the Brazilian Louros recommended them for many purposes where Teak has previously been found satisfactory as well as for durable construction, flooring, and millwork.

4. Goncalo Alves (Astronium graveolens). This species is a common tree in the upland forests from Mexico and Central America through Ecuador, Colombia, Venezuela, and Brazil. Gonçalo alves attains diameters of 2-3 feet or more and a maximum height of 120 feet. Except for narrow buttress flanges extending upward from the ground for several feet, the tree commonly has a clear symmetrical bole for two-thirds of its height.

The wood of Gonçalo Alves is very heavy, averaging 63 pounds per cubic foot when air dry. Strength is not high in proportion to its weight but is nevertheless greater than that of White Oak particularly in compression both along and across the grain. Shrinkage is appreciably less than that of Oak, weathering qualities excellent, and the heartwood is highly resistant to decay.

The wood is used in the tropics for flooring and general construction and its properties indicate suitability for durable construction.

Moderately strong woods (Southern Pine--Douglas Fir class)

1. Yellow Sanders (Buchenavia capitata). This species attains its best development in the West Indies and on the northern edge of South America. Closely related species are found in the Amazon valley. Yellow Sanders reaches a diameter of 3 feet and a height of 80 feet. Log form is good above a basal buttress.

The wood is slightly heavier than Longleaf Pine but most strength properties of Yellow Sanders are intermediate to those of Longleaf Pine and Douglas Fir. Shrinkage is exceedingly low, nearly comparable to that of Teak, and the wood shows good resistance to checking upon weathering. Decay resistance is very high. Tests in Hawaiian waters indicate that the wood lacks resistance to marine borers (4).

Although present local use of Yellow Sanders is limited mainly to furniture, the wood has much to recommend its use in boat construction, flooring, and durable construction.

2. Angelino Aceituno (Nectandra concinna). This species is a medium-sized timber-yielding tree native to Costa Rica, Colombia, and Venezuela. Little specific information is known concerning its abundance or availability.

The wood is comparable to Longleaf Pine in density and strength. Shrinkage is low and weathering characteristics good. Heartwood is rated as very durable in resistance to decay organisms. Its moisture absorption is low, comparable to Teak. These properties together with its local use in tropical construction recommend Angelino Aceituno for durable construction as well as for many uses in boat and ship construction.

3. Andiroba (Carapa guianensis). This species is found over a wide range from British Honduras and the West Indies south through Brazil and Peru. In view of this wide geographical distribution, it is suggested that the data reported here should be limited to timber from the Amazon region, the source of the test material. Trees are straight and of good form, commonly 2-3 feet in diameter and 80-100 feet in height. Buttresses are low, leaving a clear bole length of 50 feet or more. Andiroba reaches its best development and is most abundant in the Amazon flood plains, on alluvial flats, and scattered along water courses. During a 6-month period, 12 per cent of the cut at a large sawmill on the Rio Tapajos is reported to have been Andiroba.

Andiroba is comparable to Longleaf Pine in density and most strength properties. It compares with Douglas Fir in compressive strength across the grain. Shrinkage is slightly less than that of Longleaf Pine. Care is required in seasoning Andiroba lumber to prevent checking and splitting, and slow drying under cover is recommended for best results in air seasoning. After it has been seasoned, however, the wood weathers well with only minor checking. Heartwood is very durable with respect to decay.

Andiroba has been used for both interior and exterior construction in the tropics and its properties recommend it for heavy durable construction.

4. Rajate Bien (Vitex Cooperi), Flor Azul (Vitex Kuylenii). These closely related species are much alike in the characteristics of their wood and are combined here for discussion. Their geographical range includes Mexico, Guatemala, Honduras, and British Honduras. Flor Azul is generally small to medium sized but Rajate Bien occasionally attains large size.

In weight per cubic foot these timbers compare with Longleaf Pine whereas their mechanical properties more nearly approach those of Douglas Fir. When air dry, stiffness is about three-fourths that of Douglas Fir, shrinkage is considerably below that of Longleaf Pine or Douglas Fir, and resistance to weathering is excellent. The wood is very durable in resisting attack by decay organisms.

In Guatemala both species are used for general and durable construction, Rajate Bien being considered the better of the two and the more widely used. The timber should be suitable for flooring, planking, and uses involving exposure to weathering.

Species Resistant to Marine Borer Attack

Tests to determine the marine borer resistance of a number of Tropical American woods were begun by the W. F. Clapp Laboratories in 1948 at Kure Beach, North Caroline. A second series of specimens, together with a number of domestic woods, was exposed at the same site in June 1949 and supplemented by additional tropical woods in August 1949. In April 1950, the test panels were transferred to Harbor Island, North Carolina, where the tests are continuing. The most recent inspection for which results are shown in Table 2 was made in July 1951. Since that time specimens of a considerable number of species have been submitted for testing as shown in Table 2 although, of course, no data concerning their resistance are yet available.

Resistance ratings for 25 tropical woods and a few domestic woods, summarized from reports of the Clapp Laboratories (1, 2), are shown in Table 2. At each inspection period following 10-12 months, 16 months, and 24 months of exposure, each species was rated on the basis of the degree of resistance to attack by marine borers shown by small (2 x 3 x 18 inch) specimens of heartwood. As shown in a footnote to Table 2, ratings ranged from "A" indicating no marine borer activity to "E" representing very heavy marine borer activity. When deterioration of a specimen had progressed to a point of severe damage, it was removed from test and cut up for detailed examination.

With the exception of Redwood and Bald Cypress, all domestic woods under exposure were completely destroyed within the first 9-month period and these species, together with the tropical wood Balsa, were consequently removed from test at that time. The least resistant of the other tropical woods had failed after 12 months' exposure, a considerably larger number by 16 months, and all but five of them had been subjected to fairly heavy attack at 24 months.

Inasmuch as a majority of these tropical woods showed no effect, or only slight evidence of marine borer activity, at 12 months, it appears that this period is too short to permit of a reasonable evaluation of their resistance. At 24 months, on the other hand, species that had deteriorated at quite different rates were no longer distinguishable from one another.

Consequently, it is suggested that the results of the 16-month inspection are most suitable for the purpose of rating the resistance of individual species in these tests. It is not proposed to attempt to estimate service life of piling or timbers of structural sizes from these results on small specimens. However, it should be pointed out that Angélique (see Table 2) has an established reputation for long life in marine structures in French Guiana, France, and the Panama Canal. Little pholad and no significant _Teredo_ damage had occurred after 15 years of service in marine borer infested waters at Balboa, Canal Zone.

Interpretation of results shown in Table 2 for _Eschweilera_ sp. is assisted by the knowledge that Manbarklak (_Eschweilera longipes_) and the closely related species, _E. subglandulosa_ and _E. corrugata_, are widely recognized for their high resistance to marine borers. Manbarklak piles have been reported perfectly sound after 17 years in brackish waters in the Saramacca Canal, Surinam. This species also established the best record of a considerable number of species after 15 years of service in an experimental installation at Balboa, Canal Zone. An agency of the Netherlands government has reported piles of Manbarklak to be still sound after 75 years' service in the harbor at Nieuwediep, Holland.

Edmondson, on the basis of similar specimens, has stated, "a wood that stands up well in Honolulu Harbor, which is a severe testing ground, for one or more years rates honorable mention." (4). Several of the species included in this category in his report are also shown here in a favorable light either directly or by analogy with closely related species. Among these are _Ocotea rubra_, _Eschweilera Sagotiana_, _Eschweilera blanchetiana_, _Eschweilera tenax_, and _Lecythis usitata_.

Best performance among the 25 tropical woods under test at Harbor Island, North Carolina, based upon the results of 16 months' exposure, is shown by the following:

Acapú (_Vouacapoua americana_)
Morrão (_Eschweilera blanchetiana_)
Sapucaia (_Lecythis usitata_)
Angélique (_Dicorynia paraensis_)
Determa (_Ocotea rubra_)
Coco de Mono (_Eschweilera tenax_)
Cumaru Preto (_Taralea sp._)
Black Kakeralli (_Eschweilera Sagotiana_)

Natural marine borer resistance of wood has been ascribed commonly to its silica content. The woods of this study have been analyzed for total ash and silica content in three separate series of tests conducted at the

Institute of Paper Chemistry (9), the Connecticut Agricultural Experiment Station, and Yale School of Forestry (7). Results of these incomplete tests are summarized in Table 2. No specific correlation between silica content and marine borer resistance has been attempted inasmuch as samples for chemical analysis were not necessarily obtained from the same logs nor even from the same country of origin as were the exposure specimens. In a number of instances, chemical analyses were conducted upon composite samples of sawdust representing a mixture obtained from several different sources.

Total ash content which generally amounts to less than 0.5 per cent of oven-dry weight for domestic woods is seen to range as high as 2 per cent in some of these woods. In those woods for which spectrographic data on silicon in the ash are available, this element is seen to vary from weak to very strong, in the latter instances amounting to one-half to two-thirds of the total ash when expressed as silica (SiO_2) as shown in the chemical analysis. It should be borne in mind that the spectrographic technique used here permits only of an estimation of the proportionate amount of silica in the total ash content. A strong indication of silicon in the ash of a species such as Greenheart, which is extremely low in ash, would therefore not be as significant as a strong line in a wood like Teak which is high in total mineral content.

In the chemical analyses, silica is expressed as a percentage of oven-dry weight, ranging from 0.000 to 1.51 per cent among these species. Unfortunately these studies are not yet complete and only limited data are presently available. However, when allowance is made for variability within a species from one source to another, the evidence appears to confirm the reputed influence of silica content upon marine borer resistance. Of several species that consistently show a silica content of 0.20 per cent or more in these analyses including Angélique, Teak, and Black Kakeralli, only Teak was found not to have a favorable degree of resistance to borers. Wise (9) cites the work of Bromley and Rudge to indicate the wide variation in mineral content of Teak. On the basis of analyses of ten samples of this species, variation in total ash was found to range from 0.64 to 4.3 per cent with a silica range of 0.03 to 3.0 per cent.

Looking at the negative side of this relationship, however, a number of the resistant species such as Acapú, Determa, and the well-known Greenheart are extremely low in silica and therefore must owe their resistance to other factors. Variability may be involved here too. A specific example is that of Acapú (Vouacapoua americana) which was found by Edmondson to be lacking in marine borer resistance in Hawaii (4). In the case of Greenheart, Wise has suggested that resistance to Teredo may be due to the appreciable amounts of alkaloidal material present in the wood (9).

It would appear to be reasonable to anticipate favorable marine borer resistance for woods characterized by high silica content, even though resistance is not exclusively dependent upon silica content. High density of a wood is not an appreciable deterrent to marine borer activity as evidenced by

the rapid deterioration of Bulletwood in these tests and of Licaria canella in tests conducted by Edmondson in Hawaii.

A number of woods listed in Table 2 for which exposure data are not yet available would appear on the basis of their silica content to be highly resistant to attack. Among such woods are Licania buxifolia, Parinari excelsa, Licania macrophylla, Eschweilera odora, Parinari Rodolphi, Parinari campestris, and Eschweilera subglandulosa.

The following paragraphs briefly describe the species that have shown best performance to date in these marine borer exposure tests. These species are arranged in approximate order of indicated resistance. While showing good resistance to marine borers, several of these species are not outstanding in their resistance to decay, suggesting the possibility that longer service life may be obtainable from them if they were given a preservative treatment to improve their performance in this respect.

1. Acapú (Vouacapoua americana). See description under Species Suitable for Above-Water Construction.

2. Morrão (Eschweilera blanchetiana). This is one of about 80 species of medium-sized to very large trees of the genus Eschweilera occurring from eastern Brazil through the Amazon basin to Trinidad and Costa Rica. Little specific information is available concerning the abundance or distribution of Morrão, but the material used in these tests originated near Belém, Brazil. The wood appears to share the general characteristics of the Manbarklak group of Eschweilera. These timbers are extremely hard and strong with air-dry weights of 69-78 pounds per cubic foot. The wood is difficult to work and highly durable with respect to decay and, as noted previously in this paper, with an outstanding reputation for marine borer resistance. Record and Hess (6) report that the only damage to Manbarklak after years of service in brackish waters infested by Neoteredo was a slight superficial injury inflicted by the marine stone borer, Martesia cuneiformis.

3. Sapucaia (Lecythis usitata). The genus Lecythis includes a large number of imperfectly known species which are widely distributed from southeastern Brazil through northern South America to Costa Rica. The name Sapucaia is applied to most of the Brazilian species of Lecythis. These trees are common in both the Amazon lowlands and the coastal mountains. The trees are large, often reaching 5-6 feet in diameter with buttressed boles extending free of branches for 50-60 feet.

The wood of Sapucaia is typically very hard, strong, and heavy, weighing from 53-69 pounds per cubic foot when air dry. The timbers of this group vary from fair to excellent in decay resistance. They are used in heavy construction, in bridges, and as railway crossties in Brazil.

4. Angélique (Dicorynia paraensis). This tree is abundant in Surinam, French Guiana, and the Brazilian Amazon. It is reported to be one of the most common of the larger trees along the Rio Negro. The tree of Angélique is large, attaining diameters of 5 feet or more and heights up to 150 feet.

The wood compares favorably with Teak in its mechanical properties and is comparable to Teak in density. It is moderate in shrinkage and fair in its weathering characteristics as shown in Table 1. The wood is durable with respect to decay although not exceptionally so. Its reputation for high marine borer resistance has been referred to previously. These properties particularly recommend the use of Angélique for marine piling and submerged construction in marine borer infested waters, although it also appears to be suitable as a Teak replacement for many purposes including boat and ship decking.

5. Determa (Ocotea rubra). This species, which is related to Greenheart (Ocotea Rodiaei) but is not similar to it, occurs throughout the lowlands of the Guianas and the lower Amazon region. The tree is large and straight-boled reaching diameters of 3-4 feet, heights of 100 feet or more, and is free of branches for 40-70 feet.

The wood is lighter and weaker than White Oak as shown in Table 1. Shrinkage is moderate and weathering characteristics excellent. The wood is durable with respect to decay, although not outstanding in this respect, and is used in the tropics for both interior and exterior construction. Its comparative softness is not favorable for uses involving abrasion or heavy wear. In addition to its favorable resistance to marine borers shown in these tests, Determa did not deteriorate appreciably when subjected to marine borer attack in Honolulu Harbor for 13 months (4). The wood contains no significant quantity of silica but does include considerable quantities of a characteristic wax (9).

6. Coco de Mono (Eschweilera tenax). Coco de Mono is the name commonly applied in Venezuela to species of the genus Eschweilera. The wood used in these tests originated in the state of Portuguesa, Venezuela. The general properties of the Manbarklak group of the genus Eschweilera, as given in the description of Morrão, are believed to apply to this species as well.

7. Cumaru Preto (Taralea sp.). No specific information is available concerning the particular species in these tests. It is presumably one of several species of the genus Taralea which includes medium-sized to rather large trees in the Amazon basin and possibly in eastern Peru, Venezuela, and the Guianas. The wood is extremely hard and strong. Its air-dry weight is about 75 pounds per cubic foot. Decay resistance is presumed to be excellent, and the timber is suitable for heavy durable construction but not utilized at present to any extent.

8. Black Kakeralli (Eschweilera Sagotiana). This species is closely related to the Manbarklak previously referred to. Although at least 15 species of Eschweilera, all known as Kakeralli, grow in British Guiana, at least three-fourths of the total volume in most areas consists of Black Kakeralli. It is found throughout most of the climax rain forests of British Guiana but is most abundant in the western districts. These trees frequently attain diameters of 2 feet or more and heights of 100 feet. Buttresses are small or absent. Timbers squared to 12 inches and 40 feet long, and round piling up to 60 feet long, are obtainable.

The wood is very heavy, weighing 63 pounds per cubic foot when air dry. Its strength properties approach those of Greenheart as shown in Table 1. The wood is highly decay resistant but prone to split and check upon weathering. In addition to the marine borer resistance shown in these tests, Black Kakeralli was only lightly attacked during 24 months of exposure to marine borers in Hawaii (4). Its strength, resistance to decay, and resistance to marine organisms adapt this wood to heavy durable construction both above water and submerged. When used as piling it may be desirable to cap the butt end to avoid splitting.

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Table 1. Comparison of selected Tropical American woods from the standpoint of their adaptability to durable waterfront construction.

Species		Condition	Weight lb. per cu. ft.	Modulus of Rupture p.s.i	Modulus of Elasticity 1000 p.s.i.	Maximum Crushing Strength p.s.i	Compression ⊥ Grain p.s.i
Greenheart (*Ocotea Rodiaei*)	Br. Guiana	Green	78	19,550	2,970	10,160	2,040
		Air Dry	68	25,500	3,700	12,920	1,970
Almendro (*Coumarouna oleifera*)	Panama, Brazil	Green	81	17,950	2,690	8,600	1,970
		Air Dry	67	25,840	3,120	13,660	2,400
Cumaru (*Coumarouna odorata*)							
Bulletwood (*Manilkara bidentata*)	Surinam, Br. Guiana, Puerto Rico	Green	78	17,310	2,700	8,690	2,480
		Air Dry	66	27,280	3,450	11,640	2,320
Goncalo Alves (*Astronium graveolens*)	Honduras, Venezuela	Green	76	12,140	1,940	6,590	1,840
		Air Dry	63	16,620	2,230	10,320	2,110
Black Kakeralli (*Eschweilera Sagotiana*)	Br. Guiana	Green	77	17,780	2,910	7,780	1,580
		Air Dry	63	23,420	3,250	11,210	1,530
Guayacán (*Tabebuia guayacan*, (*T. heterotricha*)	Honduras, Panama	Green	71	19,280	2,350	8,710	1,910
		Air Dry	62	24,890	2,640	11,700	2,280
Acapú (*Vouacapoua americana*)	Surinam	Green	79	16,560	2,600	9,700	2,070
		Air Dry	59	--	--	--	--
Muira-juba (*Apuleia molaris*)	Brazil	Green	74	15,360	2,180	7,330	1,690
		Air Dry	57	20,960	2,510	10,530	2,040
Piquiá (*Caryocar villosum*)	Brzil	Green	72	12,450	1,820	6,290	2,080
		Air Dry	55	17,060	2,160	8,410	1,620
Mylady (*Aspidosperma cruentum*)	Br. Honduras	Green	70	14,100	2,500	6,650	1,100
		Air Dry	53	20,790	2,760	11,110	1,320

Species	Shrinkage Radial, pct.	Shrinkage Tangential, pct.	Weathering Resistance to Checking & Splitting /1	Decay Resistance /2	Marine Borer Resistance /3 10-12 months	16 months	24 months
Greenheart (*Ocotea Rodiaei*)	8.2	9.0	-	-	B(6 mo.)	-	-
Almendro (*Coumarouna oleifera*) Cumarú (*Coumarouna odorata*)	5.0	7.6	I	A	-	-	-
Bulletwood (*Manilkara bidentata*)	6.3	9.4	III	A	D	E	-
Gonçalo Alves (*Astronium graveolens*)	4.0	7.6	I	AA	-	-	-
Black Kakeralli (*Eschweilera Sagotiana*)	4.9	10.5	IV	AA	B	C-D	D
Guayacán (*Tabebuia guayacan*, *T. heterotricha*)	6.2	8.6	III	AA	-	-	-
Acapú (*Vouacapoua americana*)	4.0	5.8	-	AA	A	A	B
Muira-juba (*Apuleia molaris*)	4.6	6.8	I	A	-	-	-
Piquiá (*Caryocar villosum*)	5.0	8.0	III	A	-	-	-
Mylady (*Aspidosperma cruentum*)	5.2	8.7	III	AA	-	-	-

Species	Source	Condition	Weight lb.per cu.ft.	Modulus of Rupture p.s.i	Modulus of Elasticity 1000 p.s.i.	Maximum Crushing Strength p.s.i	Compression ⊥ Grain p.s.i.
Courbaril (Hymenaea courbaril)	Honduras Surinam, Puerto Rico, Panama	Green	70	12,940	1,840	5,800	1,640
		Air Dry	52	19,400	2,160	9,510	1,880
Mora Amarilla (Chlorophora tinctoria)	Guatemala, Honduras, Venezuela	Green	73	14,840	1,590	6,860	1,800
		Air Dry	52	19,560	2,160	11,080	1,940
Tatajuba (Bagassa guianensis)	Brazil	Green	67	14,510	2,300	7,900	1,200
		Air Dry	50	20,050	2,580	11,560	1,690
Nargusta (Terminalai amazonia)	Br. Guiana, Br. Honduras, Panama	Green	71	12,130	2,010	5,530	1,060
		Air Dry	50	17,750	2,300	9,540	1,230
White Oak (Quercus alba)	United States	Green	62	8,300	1,250	3,560	830
		Air Dry	48	15,200	1,780	7,440	1,320
Brazilian Louro (Aniba Duckei, A. cf. riparia, Ocotea sp.)	Brazil	Green	60	13,250	2,170	6,560	1,060
		Air Dry	47	19,030	2,570	10,010	1,110
Angélim dos Amarelos (Hymenolobium excelsum)	Brazil	Green	63	14,410	2,000	7,440	1,340
		Air Dry	46	--	--	--	--
Angélique (Dicorynia paraensis)	Surinam	Green	67	11,410	1,840	5,590	1,000
		Air Dry	45	17,390	2,190	8,770	1,280
Yellow Sanders (Buchenavia capitata)	Puerto Rico	Green	62	10,050	1,460	5,130	1,070
		Air Dry	44	12,970	1,650	7,440	1,280
Brazil Nut (Bertholletia excelsa)	Brazil	Green	62	9,740	1,610	4,530	850
		Air Dry	44	14,680	1,760	6,890	890

Species	Shrinkage Radial, pct.	Shrinkage Tangential, pct.	Weathering Resistance to Checking & Splitting/1	Decay Resistance/2	Marine Borer Resistance/3 10-12 months	Marine Borer Resistance/3 16 months	Marine Borer Resistance/3 24 months
Courbaril (*Hymenaea courbaril*)	4.5	8.5	IV	A	A	E	-
Mora Amarilla (*Chlorophora tinctoria*)	3.4	5.4	I	AA	A	D	E
Tatajuba (*Bagassa guianensis*)	5.2	6.6	IV	AA	A	D	E
Nargusta (*Terminalia amazonia*)	4.8	7.9	III	A	D	E	-
White Oak (*Quercus alba*)	5.3	9.0	II	B	E	-	-
Brazilian Louro (*Aniba Duckei*, *A.* cf. *riparia*, *Ocotea* sp.)	4.6	7.0	I	AA	-	-	-
Angelim dos Amarelos (*Hymenolobium excelsum*)	3.7	6.0	I	AA	-	-	-
Angélique (*Dicorynia paraensis*)	4.6	8.2	III	B	A	B	C
Yellow Sanders (*Buchenavia capitata*)	2.8	5.7	II	AA	-	-	-
Brazil Nut (*Bertholletia excelsa*)	3.9	8.3	II	A	-	-	-

Species	Source	Condition	Weight lb. per cu. ft.	Modulus of Rupture p.s.i.	Modulus of Elasticity 1000 p.s.i.	Maximum Crushing Strength p.s.i.	Compression ⊥ Grain p.s.i.
Teak (*Tectona grandis*)	Burma	Green	55	11,380	1,580	5,490	1,040
		Air Dry	43	13,770	1,670	7,520	1,190
Angelino Aceituno (*Nectandra concinna*)	Venezuela	Green	66	10,440	1,540	5,020	710
		Air Dry	42	14,230	1,650	7,260	1,140
Andiroba (*Carapa guianensis*)	Brazil	Green	60	11,110	1,560	4,930	960
		Air Dry	41	15,620	1,850	7,900	850
Longleaf Pine (*Pinus palustris*)	United States	Green	55	8,700	1,600	4,300	590
		Air Dry	41	14,700	1,990	8,440	1,190
Determa (*Ocotea rubra*)	Surinam, Br. Guiana	Green	61	7,820	1,460	3,760	550
		Air Dry	41	10,470	1,820	5,600	640
Rajate Bién (*Vitex Cooperi*) Flor Azul (*Vitex Kuylenii*)	Honduras, Guatemala	Green	66	9,420	1,490	4,780	1,180
		Air Dry	40	12,890	1,570	7,010	990
Tauary (*Couratari pulchra*)	Brazil, Br. Guiana	Green	53	9,240	1,730	4,260	560
		Air Dry	37	13,520	1,800	7,460	860
Douglas Fir (*Pseudotsuga taxifolia*)	United States	Green	38	7,600	1,550	3,890	510
		Air Dry	34	11,700	1,920	7,420	910

Species	Shrinkage: Radial, pct.	Shrinkage: Tangential, pct.	Weathering Resistance to Checking & Splitting /1	Decay Resistance /2	Marine Borer Resistance /3: 10-12 months	16 months	24 months
Teak (*Tectona grandis*)	2.3	4.2	I	AA	B	D	D
Angelino Aceituno (*Nectandra concinna*)	3.4	6.0	II	AA	-	-	-
Andiroba (*Carapa guianensis*)	3.1	7.6	II	A	-	-	-
Longleaf Pine (*Pinus palustris*)	5.1	7.5	-	-	E	-	-
Determa (*Ocotea rubra*)	3.7	7.7	I	B	A	B	C
Rajate Bien (*Vitex Cooperi*) Flor Azul (*Vitex Kuylenii*)	3.2	6.4	I	A	-	-	-
Tauary (*Couratari pulchra*)	4.1	7.3	III	B	B	D	D
Douglas Fir (*Pseudotsuga taxifolia*)	5.0	7.8	-	A	E	-	-

/1 I-Excellent; II-Good; III-Fair; IV-Poor

/2 AA-Average weight loss less than 3 per cent; A-Average weight loss 3-10 per cent; B-Average weight loss 11-24 per cent.

/3 A-No marine borer activity; B-Light marine borer activity; C-Moderate marine borer activity; D-Fairly heavy marine borer activity; E-Very heavy marine borer activity.

Table 2. Marine-borer exposure ratings and analyses for mineral content of Tropical American woods.

Species	Source	Specific Gravity green vol. basis	Resistance Rating[1] after Exposure for 10-12 mos.	16 mos.	24 mos.	Total Ash percentage of over-dry weight	Silica: Chemical Analysis percentage of oven-dry weight	Silica: Spectrographic Intensity in Ash
Tatajuba (*Bagassa guianensis*	Brazil	0.68	A	D	E	--	--	--
Mora Amarilla (*Chlorophora tinctoria*	Venezuela	0.71	A	D	E	1.43[2]	0.002[2]	--
Tauary (*Couratari oblongifolia*)	Brazil	--	B	D	D	--	--	--
Tauary (*Couratari pulchra*)	Brazil,) British) Guiana)	0.50	B	D	D	0.96[2]	0.078[2]	--
						0.83[3]	0.2[illegible][3]	Strong[3]
		--				1.01[4]	0.215[4]	--
	British Guiana	--	-	-	-	0.49[4]	0.113[4]	--
Angélique (*Dicorynia paraensis*)	Surinam	0.60	A	B	C	0.40[2]	0.34[2]	
						0.64[3]	0.46[3]	Very Strong[3]
						0.52[4]	0.396[4]	--
Sapupira (*Diplotropis purpurea*)	Brazil	--	A	E	-	--	--	--
	Surinam	--	-	-	-			
Morrão (*Eschweilera blanchetiana*)	Brazil	--	A	B	B	--	--	--

Species	Source	Specific Gravity green vol. basis	Resistance Rating /1 after Exposure for 10-12 mos.	16 mos.	24 mos.	Total Ash	Silica: Chemical Analysis percentage of over-dry weight	Silica: Spectrographic Intensity in Ash
Black Kakeralli (_Eschweilera Sagotiana_)	British Guiana	0.82	B	C-D	D	0.63 /3 0.49 /4	0.18 /3 0.221 /4	Strong /3 --
Coco de Mono (_Eschweilera tenax_)	Venezuela	--	A-B	C	D	1.60 /4	0.079 /4	--
Courbaril (_Hymenaea courbaril_)	Panama, Surinam	0.71	A	E	--	0.60 /2 0.85 /3	0.002 /2 --	-- Weak /3
Br. Guiana Courbaril (_Hymenaea Davisii_)	British Guiana	0.67	D	E	--	--	--	--
Sapucaia (_Lecythis usitata_)	Brazil	--	A	B	B	--	--	--
Hububalli (_Loxopterygium Sagotii_)	British Guiana	0.56	D	E	--	--	--	--
Bulletwood (_Manilkara bidentata_)	British Guiana	0.85	D	E	--	0.48 /2 0.54 /3	0.060 /2 --	-- Weak /3
Balsa (_Ochroma lagopus_)	Ecuador	0.12	D	E	--	--	--	--

Species	Source	Specific Gravity green vol. basis	Resistance Rating[1] after exposure for 10-12 mos.	16 mos.	24 mos.	Total Ash percentage of oven-dry weight	Silica: Chemical Analysis percentage of oven-dry weight	Silica: Spectrographic Intensity in Ash
Greenheart (*Ocotea Rodiaei*)	British Guiana	0.88	B(6 mo.)	--	--	0.19[3]	--	Strong[3]
Determa (*Ocotea rubra*)	Surinam	0.52	A	B	C	0.30[2] 0.19[3]	0.000[2] --	-- Weak[3]
Timborana (*Piptadenia suaveolens*)	Brazil	--	A	D	D	--	--	--
Faveiro (*Pithecolobium elegans*)	Brazil	--	B	E	--	--	--	--
Uchi (*Sacoglottis uchi*)	Brazil	--	A	D	E	--	--	--
Mahogany (*Swietenia macrophylla*)	Central America Brazil	0.45 --	A --	E --	-- --	0.59[3] 0.62[4]	0.018[3] 0.049[4]	Weak to medium[3] --
Cumaru Preto (*Taralea* sp.)	Brazil	--	B	C	D	--	--	--
Teak (*Tectona grandis*)	Burma	0,58	B	D	D	1.40[3] 1.81[4]	0.64[3] 0.892[4]	Very strong[3] --
Nargusta (*Terminalia amazonia*)	British Buiana	0.64	D	E	--	0.62[2]	0.012[2]	--

Species	Source	Specific Gravity green vol. basis	Resistance Rating/1 after Exposure for 10-12 mos.	16 mos.	24 mos.	Total Ash percentage of oven-dry weight	Silica: Chemical Analysis percentage of oven-dry weight	Silica: Spectrograph Intensity in Ash
Fiddlewood (*Vitex Gaumeri*)	British Honduras	0.56	A	C	D	0.82/2	0.025/2	--
Acapú (*Vouacapoua americana*)	Surinam	0.78	A	A	B	0.51/4	0.002/4	--
So. Yellow Pine (*Pinus* sp.)	United States	0.54	E	--	--	--	--	--
Douglas Fir (*Pseudotsuga taxifolia*)	United States	0.45	E	--	--	--	--	--
White Oak (*Quercus alba*)	United States	0.60	E	--	--	--	--	--
Redwood (*Sequoia sempervirens*)	United States	0.38	C	--	--	--	--	--
Bald Cypress (*Taxodium distichum*)	United States	0.42	C	--	--	--	--	--
Freijo (*Cordia Goeldiana*)	Brazil	--	--	--	--	--	--	--
Manbarklak (*Eschweilera subglandulosa*)	Surinam	--	--	--	--	1.22/4	0.688/4	--

Species	Source	Specific Gravity green vol. basis	Resistance Rating[1] after Exposure for 10-12 mos.	16 mos.	24 mos.	Total Ash percentage of oven-dry weight	Silica Chemical Analysis	Silica Spectrographic Intensity in Ash
Mata-mata (*Eschweilera odora*)	Brazil	--	--	--	--	1.18[4]	0.619[4]	--
Kopie (*Goupia glabra*)	Surinam	--	--	--	--	0.80[4] 0.42[4]	0.057[4] 0.034[4]	-- --
Jarana (*Holopixidium jarana*)	Brazil	--	--	--	--	0.75[4]	0.087[4]	--
Angelim dos Amarelos (*Hymenolobium excelsum*)	Brazil	0.62	--	--	--	0.37[2]	0.002[2]	--
Sapucaia (*Lecythis paraensis*)	Brazil	--	--	--	--	0.41[4]	0.048[4]	--
Marishiballi (*Licania buxifolia*)	British Guiana	--	--	--	--	0.88[4]	0.432[4]	--
Anaura (*Licania macrophylla*)	Brazil, Surinam	--	--	--	--	1.94[4] 2.01[4]	1.51[4] 1.54[4]	-- --
Kaneelhart (*Licaria cavennensis*)	British Guiana	1.03	--	--	--	0.08[2] 0.03[3]	0.00[2] --	-- Medium[3]
Manu (*Minquartia guianensis*)	Costa Rica	--	--	--	--	0.93[4]	0.034[4]	--

Species	Source	Specific Gravity	Resistance Rating [1] after Exposure for			Total Ash percentage of oven-dry weight	Silica	
			10-12 mos.	16 mos.	24 mos.		Chemical Analysis	Spectrographic Intensity in Ash
Ucuuba-rana (*Osteophloeum platyspermum*)	Brazil	--	--	--	--	--	--	--
Witte Foengoe (*Parinari campestris*)	Surinam	--	--	--	--	1.29 [4]	0.902 [4]	--
Aiomoradon (*Parinari excelsa*)	British Guiana	--	--	--	--	1.05 [4]	0.576 [4]	--
Parinari (*Parinari Rodolphi*)	Brazil	--	--	--	--	1.09 [4]	0.804 [4]	--
Pau d'arco (*Tabebuia serratifolia*)	Brazil, Surinam	--	--	--	--	--	--	--

[1] A--No marine borer activity; B--Light marine borer activity; C--Moderate marine borer activity; D--Fairly heavy marine borer activity; E--Very heavy marine borer activity.

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